48th ANNUAL MEETING OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVII MAY 1952 No. 5

CONTENTS:

Francis R. Mosbaugh—Obituary - - - - - - - - 306

William S. Calcott—Obituary - - - - - - - - 307

H. Webster Thomas—Obituary - - - - - - - - 307

Minutes of Supervisory Committee on Tannin Analysis *By* J. F. WAGONER - - - - - - - - - - - - 307

Council Meeting Minutes - - - - - - - - - 308

Comparative Balance Sheet of the Association for 1951 - 309

Effects of Tannery Processes on the Electronscopic Appearances of Bovine Hide Collagen Fibrils *By* R. BORASKY and J. S. ROGERS - - - - - - - - - - - - - 312

Influence of Splitting on the Strength of Chrome Tanned Steer Sides *By* J. R. KANAGY - - - - - - - - 329

Sampling of Side Upper Leather *By* C. W. MANN - - 352

Book Notices - - - - - - - - - - - - - 371

Abstracts - - - - - - - - - - - - - - 372

Patents - - - - - - - - - - - - - - - 377

SUBSCRIPTION: Members $12.00 a Year Non-Members $15.00

Published Monthly by

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLICATION OFFICE, EASTON, PA.

Entered as Second-Class Matter at Post Office, Easton, Pa.
Acceptance for Mailing at Special Rate of Postage as Provided for in Section 1103.
Act of October 3, 1917, Authorized July 16, 1918

COPYRIGHT, 1952, THE AMERICAN LEATHER CHEMISTS ASSOCIATION

NEW OCEAN HOUSE, SWAMPSCOTT, MASS. June 1, 2, 3, and 4, 1952

Reliable Direct Sources the World Over

FOR

VEGETABLE TANNING MATERIALS

WATTLE EXTRACT
WATTLE BARK
MANGROVE BARK
MYRABOLAMS & EXTRACT
VALONEA & EXTRACT
DIVI DIVI
CUTCH
QUEBRACHO
SUMAC—LEAF & GROUND
TARA—PODS & POWDER
OAKWOOD EXTRACT, Swedish
LARCHBARK EXTRACT, Swedish

The OLSON SALES AGENCY

Import · Export

20 BROAD STREET (NEAR WALL STREET) NEW YORK 5, N. Y.

Cable Address:
"COROSAGE"

Telephones:
DIGBY 4-0226
0227

On the Job for 86 Years!

Almost a century ago—1866—we developed the first Gargoyle product for tanners... a harness oil made from petroleum. Since then we have worked hand in hand with tanners to help them make good leather.

Today we offer you our research facilities... the services of leather chemists and of field technicians who are specialists in leather oils and their correct application... our line of Gargoyle leather oils, greases and specialties, all made under the most exacting standards to assure top quality.

Our 86 years' experience, technical facilities and products can help improve your position. Give us a call.

SOCONY-VACUUM

QUALITY AND SERVICE SINCE 1866

SOCONY-VACUUM OIL CO., INC., TANNERS DIVISION, 26 BROADWAY, NEW YORK 4, N. Y.

GARGOYLE LEATHER OILS and GREASES

SPRUCE EXTRACT

POWDERED SUPER SPRUCE

LACTANX

■

Robeson Process Company

General Offices: 500 Fifth Avenue, New York, N. Y.

Operating Plant at Erie, Pa.

MECO EXTRACT

ONE GRADE—THE BEST

CHESTNUT WOOD EXTRACT

All Concentrations, Liquid to Dry Powder

Teas Extract Co.

6400 Centennial Boulevard

NASHVILLE 9, TENNESSEE

TENNESSEE PLANT
Nashville, Tenn.

ANDREWS PLANT
Andrews, N. C

Sterozol

Reliable Germicide and Preservative

Sterozol is a non-coloring, non-interfering liquid which can be used in any wet operation:

- For inhibiting microbial action on hides and skins in process
- For inhibiting mold on stock and leather in process
- For preserving finishes

Sterozol's low relative toxicity, ease of handling, and economy have contributed in a large measure to its acceptance in the trade.

Sebacol

. . . for dependable unhairing

Sebacol produces clean, uniform, quality leather under varied beam-house practices.

Biobate

. . . for effective bating

Biobate provides controlled, effective enzymatic action during bating for all types of leather.

WALLERSTEIN COMPANY, INC.

180 MADISON AVENUE · NEW YORK 16, N. Y.

To bring out the best in your leather...

Specify Cyanamid Tanning Specialties

TANAK® Synthetic Tanning Agents, the time-tested naphthalene type syntans, are ideal for imparting better performance qualities to leather products that must withstand severe usage or wear. Whether it's *chrome tanning*, where a uniform, fine grain leather is desired... or *vegetable tanning*, where fast penetration of the tannins is required ... TANAK can help you get effective results.
Let our staff help you make tests.

Other performance-proved Cyanamid Tanning Specialties include:

CUTRILIN® Bates ... the pancreatic "bates of choice" in the tanning industry.

TWECOTAN® Tanning Extracts* ... blends to meet specific tanning requirements.

DYEWOODS and Extracts* ... a full line for every important need.

TANAK® MRX Tanning Agent ... widely preferred by experienced tanners for upgrading white and colored leathers.

BETASOL® OT Wetting Agent ... most powerful wetting agent available for tanning.

Write today for complete information on any of these products.

AMERICAN Cyanamid COMPANY

INDUSTRIAL CHEMICALS DIVISION
30 Rockefeller Plaza, New York 20, N. Y.

In Canada: North American Cyanamid Limited, Toronto and Montreal

*Made by Taylor White Extracting Company—Cyanamid sole distributors.

ARKO FAT LIQUORS

FORMULATED FOR PERFECT TAKE-UP AND NOURISHMENT

ARKO FAT LIQUOR L M:—Especially made for horsehide, cow sides glove and garment leather. Excellent for goatskin glove and garment.

ARKO FAT LIQUOR L C:—A superior oil for deer, pig, cape and cabretta glove leather.

ARKO FAT LIQUOR C B:—Processed sulfonated cod oil for vegetable leathers.

ARKO FAT LIQUOR D:—For very fine suede leathers where dryness, nourishment and stretch are required.

Information, samples and demonstration upon request.

ARKANSAS COMPANY, Inc.
Newark, N. J.

Manufacturers of Industrial Chemicals for over 45 years

Better Leathers at Lower Cost ...

It's Easy With *Linco Products*

LINCO PRODUCTS

●

PANCREATIC BATES
FILLERS
SOLE LEATHER FINISHES
TANNER'S LIME
AND CHEMICALS

Do you believe the maintaining of leather markets desirable? If so, highest quality leathers at lowest possible cost are necessary. To accomplish this, no single improvement can be the answer but a lot of steps in the right direction might. Better yields is a very important step.

We invite your inquiries and permission to prove better yields with LINCO PRODUCTS.

L. H. LINCOLN & SON, inc.

COUDERSPORT, PA.

MANUFACTURERS AND DISTRIBUTORS OF TANNING MATERIALS
CONSULTANTS ON TANNING PROBLEMS

. . . STANDARDIZE ON

SUPREME QUALITY * HABU-COAT *Tannery Finishes*

FOR ANILINE, SEMI-ANILINE AND PIGMENTED EFFECTS

for all leathers

SHOE

GARMENT

GLOVE

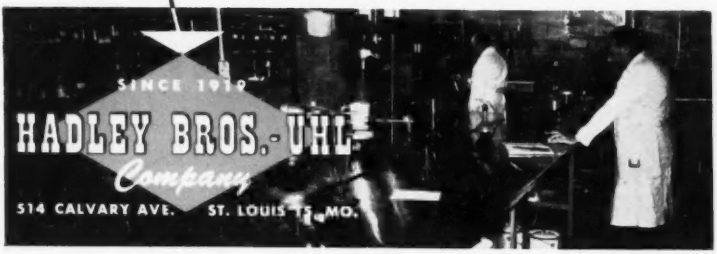
LUGGAGE

UPHOLSTERY

THEY GIVE 'CHARACTER'

For beautifying leathers of all types HABU-COAT Finishes by HADLEY'S comprise the newest formulations in any color range . . for application by swab or spray. Modern laboratory facilities assure controlled quality that meets the high standard demanded by the leather industry. All finishes are customized to your specifications. Send us your swatches.

*THEY'RE LABORATORY CONTROLLED



DYESTUFFS

for

black

grey

brown

navy

green

wine

cocoa

grain

and

suede leather

On any of your coloring problems our Technical Laboratory will be glad to cooperate with you in selecting the correct dyestuffs and proper method of application.

GENERAL DYESTUFF CORPORATION

435 HUDSON STREET, NEW YORK 14, NEW YORK

BOSTON • CHARLOTTE • CHICAGO • PHILADELPHIA • PROVIDENCE • SAN FRANCISCO

Shoe design courtesy Andrew Geller.

OUR 154th YEAR

Natural Dyewood Products

Logwood

Fustic • Hypernic • Osage Orange

Produce level bottom shades for all colored leathers

•

Tanning Extracts

Dehydrated in the modern manner, perfect solubility, lowest cost

•

Coal Tar Dyestuffs, Synthetic Tans

•

NEW YORK COLOR & CHEMICAL CO. DIVISION

BELLEVILLE, NEW JERSEY

AMERICAN DYEWOOD CO.

285 MADISON AVENUE NEW YORK 17, N. Y.

Factories:
CHESTER, PA. BELLEVILLE, N. J.

Branch Offices:
BELLEVILLE, N. J. DANVERS, MASS.
CHICAGO, ILL. PHILADELPHIA, PA.
TORONTO, CANADA
MONTREAL, CANADA

SOLVAY
Ammonium
Bicarbonate

Improves the Quality of Your Leathers

...by penetrating the leather rapidly—raising the pH uniformly throughout the thickness of the hide.
...by maintaining the grain.
...by improving dyeing characteristics.

Specify SOLVAY AMMONIUM BICARBONATE for quality leathers!

Other Products for Tanners

- **CLEANSING SODA XX**
- **SNOWFLAKE* CRYSTALS**

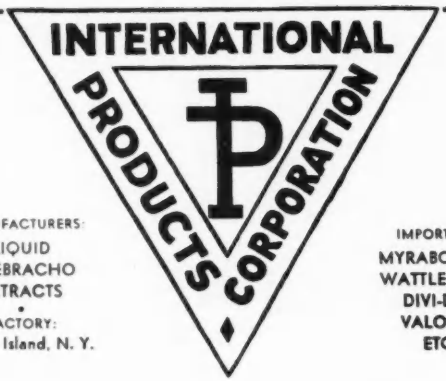
*REG. U. S. PAT. OFF.

SOLVAY Alkalies Chemicals 70 YEARS OF SERVICE 1881 1951

SOLVAY SALES DIVISION
ALLIED CHEMICAL & DYE CORPORATION
40 Rector Street, New York 6, N. Y.

BRANCH SALES OFFICES

Boston • Charlotte • Chicago • Cincinnati • Cleveland
Detroit • Houston • New Orleans • New York
Philadelphia • Pittsburgh • St. Louis • Syracuse



MANUFACTURERS:
LIQUID
QUEBRACHO
EXTRACTS
•
FACTORY:
Staten Island, N. Y.

IMPORTERS:
MYRABOLAMS
WATTLE BARK
DIVI-DIVI
VALONIA
ETC.

INTERNATIONAL PRODUCTS CORPORATION

29 BROADWAY 6, NEW YORK

Representatives:

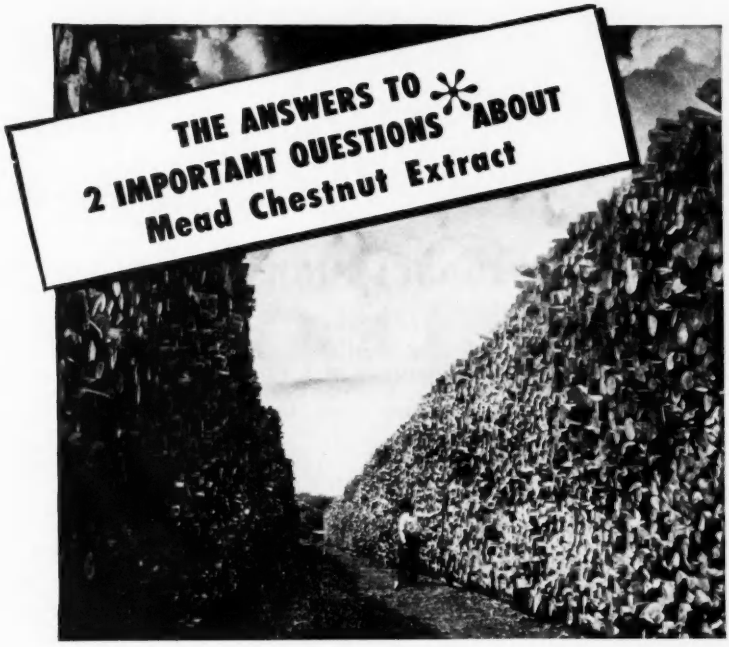
San Francisco - London, Canada - Boston
Havana, Cuba - Mexico City, Mexico

"SUPREMO"
BRAND
SOLID-ORDINARY

"LUNA"
BRAND
COLD WATER SOLUBLE

QUEBRACHO EXTRACTS

FACTORY AT PUERTO PINASCO, PARAGUAY



This is only a portion of the many stockpiles of chestnut logs that insure a continuous supply of Chestnut Extract.

1. Is the supply of Mead Chestnut Extract adequate?

Decidedly yes. Recent surveys show that there is enough chestnut wood in our forests to serve the leather industry for many years to come. Huge chestnut stockpiles, such as the one shown above, are converted under chemical control at five extract plants, insuring a steady supply of Mead Chestnut Extract.

2. Why is Mead Chestnut Extract preferred over other tanning agents?

Mead Chestnut Extract is a superior tanning material, made by America's largest producer of vegetable tanning extracts. Repeated experience has shown:

A. Chestnut tanned leathers do not oxidize, darken on exposure to light, or develop an uneven color on aging, as do leathers tanned with many other materials, vegetable or synthetic.

B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

Ask about Mead Cold Soluble Chestnut Extract for retanned leathers. And—for more pounds of plumper leather—standardize on Mead Chestnut Extract.

IT'S A FACT!

Mead Chestnut Extract will produce more pounds of plump leather per unit of tannin than any other tanning material.

Vegetable Tannin	Tan Yard Yield (*white weight basis*)
Chestnut Wood Extract	67%
Tanning Material A	61%
Tanning Material B	63%

Calculate your tanning material costs on a leather basis as well as on a tan unit basis. Mead Chestnut Extract, producing four to six pounds more leather, means positive savings.

MEAD CHESTNUT EXTRACT

THE MEAD CORPORATION
Tannin Extract Division, Lynchburg, Virginia

JACQUES WOLF

Chemicals

PRODUCE HIGH GRADE LEATHER

SYNEKTAN O-230
A liquid synthetic tannage that equals the qualities of vegetable extracts. Replaces Sumac. Used as a retan on chrome stock.

SYNEKTAN NPP
For high grade whites and pastel colors; produces full plump leather.

SYNEKTAN NCRP
Specialty syntan, used in combination with chrome tannage or in the dye bath for better grain.

TANASOL NCO
Syntan in beads, to use with extracts in the tanning and retanning operations.

TANASOL PW
Syntan in beads, to use with NCO for bleaching chrome stock and in retanning chrome stock. In the dye bath for good level colors.

FUNGIZYME BATES
Pancreatic bating salts of standard, controlled quality.

BATE A & AS For sheep skins and sole leather.

BATE B & BS For furniture leather, side leather and calf skins.

BATE C & CS For goat skins.

SULPHONATED OILS (Various Bases)

MONOPOLE OIL (For Finishing)

EMULSIFIERS AND DETERGENTS (For Good Degreasing)

Samples and information upon request.

JACQUES WOLF & CO.
Chemicals PASSAIC, N. J.

Branches:
Carlstadt, N. J.
Los Angeles, Calif.

For controlled action in Bating...

use **OROPON**

Original and standard synthetic bate, OROPON combines the action of a proteolytic enzyme with that of a deliming salt. It is uniform and sanitary and provides the tanner with a clean, standardized material whose action is *automatically controlled*. It is available in various grades to suit the many different types of leathers.

Full technical data on request.

CHEMICALS FOR INDUSTRY

ROHM & HAAS COMPANY

WASHINGTON SQUARE, PHILADELPHIA 5, PA.

OROPON is a trademark, Reg. U. S. Pat. Off. and in principal foreign countries.

AT YOUR SERVICE . . .

Let our *64 years* of specialized experience work for you . . . profitably

ATLAS
Guaranteed **OILS**

- **NEATSFOOT OILS**
- **SULPHONATED COD OILS**
- **SULPHONATED NEATSFOOT OILS**
- **SPLIT OILS**
- **MOELLONS, and many specialty Products**

ATLAS REFINERY SINCE 1887 QUALITY LEATHER OILS NEWARK, N.J.

A Name and Symbol
Pre-eminent in the Tannery Industry

● For over half a century, ATLAS has been a leader in the production of Quality Oils for the Tanning Industry, through extensive research to serve you better. ATLAS specialized research, plus many years of practical experience in the production of consistently high-quality, guaranteed oils is your assurance of uniformity to meet definite specifications. Give your leathers the "quality look" with ATLAS Oils.

ATLAS *Refinery, Inc.*
142 LOCKWOOD ST. NEWARK 5, N. J.

TANIMEX CORPORATION

39 BROADWAY **NEW YORK 6, N. Y.**

SOLE AGENTS FOR NORTH AMERICA

ORDINARY SOLID QUEBRACHO EXTRACT
CLARIFIED SOLID QUEBRACHO EXTRACT

Produced in Paraguay by:

Carlos Casado Limitada
Campos y Quebrachales Puerto Sastre S. A.
Sociedad Forestal de Puerto Guarani S. A.

▪ ▪ ▪ ▪

SOLID WATTLE EXTRACT - H.E.C. BRAND

Produced in South Africa by:

Hodgson Extract Co., Limited

▪ ▪ ▪ ▪

SPRAY DRIED TANNING POWDERS

Of extraordinarily high tannin concentration - completely and immediately soluble in cold water - ideal for drum tannage

QUEBRACHO
MIMOSA
MYROBALAN
VALONEA

Produced in England by:

Richard Hodgson & Sons Limited

▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪

Reduce your costs
Maintain quality

Outstanding control of microorganisms with SYNERGISTIC combinations of efficient bactericides and fungicides

BUCKMAN LABORATORIES, INC.

Manufacturing Chemists

Memphis 8, Tennessee

Representatives in Most Countries

MICROORGANISM CONTROL SPECIALISTS

Get Stronger, Cleaner Leathers with these HOOKER Sharpeners

Hooker Sharpeners give you *precise control* of the alkalinity and sulfidity of unhairing solutions. This means better yields of uniform high quality leather, plus savings on beamshop operations.

SODIUM SULFIDE—Na_2S

Mol. Wt. 78.1
M.P. . . . . 100°C

Light buff colored solid in flake form. Rapidly soluble in water; slightly soluble in alcohol; insoluble in ether. Also available in solid form.

ANALYSIS

Na_2S . . . . . 60 to 62%
NaCl . . . . . 1.5% Max.
Other Na Salts . . . . . 2.0% Max.
Fe . . . . . 8 ppm Max.
Cu, Ni, Cr, Mn, Pb. . . 1 ppm Max.
Water of crystallization 35% Min.

SHIPPING CONTAINERS

Steel drums . . . . 90 and 350 lbs. net

SODIUM SULFHYDRATE—NaSH

(sodium hydrosulfide)

Mol. Wt. 56.1
M.P. . . . . 55°C

Light lemon colored solid in flake form. Completely and rapidly soluble in water, alcohol and ether.

ANALYSIS

NaSH . . . . . 70 to 72%
Na_2S . . . . . 2.5% Max.
NaCl . . . . . 0.8% Max.
Na_2SO_3 and $NaHCO_3$. 0.4% Max.
Fe . . . . . 5 ppm Max.
Cu, Ni, Cr, Mn, Pb. . . 1 ppm Max.
Water of crystallization 28 to 26%

SHIPPING CONTAINERS

Lacquer-lined
steel drums . . . . 90 and 350 lbs. net

Hooker is known as a dependable supplier of Caustic Soda, Sodium Sulfide and Sodium Sulfhydrate for tanners. For a detailed discussion of the use of these Hooker Chemicals in the leather industry, write on your company letterhead for Hooker Bulletins Nos. 500, "Hooker Sodium Sulfhydrate" and 503, "Studies in Unhairing" by E. R. Theis and M. O. Ricker.

HOOKER ELECTROCHEMICAL COMPANY

3 UNION ST., NIAGARA FALLS, N. Y.
NEW YORK, N. Y. • WILMINGTON, CALIF.
TACOMA, WASH.

CHLORINE • SODIUM TETRASULFIDE • SODIUM SULFIDE
CAUSTIC SODA • MURIATIC ACID • PARADICHLOROBENZENE

HOOKER CHEMICALS ®

10-1634

QUEBRACHO EXTRACTS

SOLID	LIQUID	POWDERED
STANDARD	SM	"PUREX"
BRANDS	SMS	SMS

PLANTS: NEWARK, N. J. — PEABODY, MASS.

ALSO

Tanning Extracts and Raw Tanning Materials from all parts of the world.

MYRABOLAMS	MANGROVE BARK
DIVI DIVI	VALONEA
TARA	SUMAC

WATTLE BARK
SOLID WATTLE EXTRACT
POWDERED MANGROVE and
VALONEA EXTRACTS

—IMPORTED BY—

THE

RIVER PLATE

IMPORT AND EXPORT CORPORATION

CHRYSLER BUILDING

405 LEXINGTON AVE., NEW YORK (17), N. Y.

DEVELOPMENT AND

INTRODUCTION OF

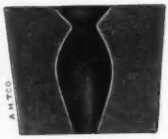
BETTER **CHEM**ICALS FOR **TAN**NING

A.H.T. CO. SPECIFICATION

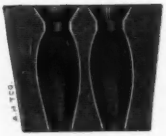
RUBBER STOPPERS HR-108

IN OUR STOCK FOR IMMEDIATE SHIPMENT

Semi-Solid.
Vertical cross-section showing recessed top.



One-Hole.
Vertical cross-section showing one Hough fusiform opening.



Two-Hole.
Vertical cross-section showing two Hough fusiform openings.

RUBBER STOPPERS HR-108, A.H.T. Co. Specification. Made of a bloomless, black, heat-resisting composition with low sulfur content and superior aging quality. The designation HR-108 originates from "Heat Resisting" and the specific gravity of the composition, i.e. 108. The stock possesses great elasticity, contains more than 70% pure virgin gum*, is free from surface sulfur and contains less than 0.75% free sulfur; no reclaimed rubber is used. Will withstand temperatures up to 110°C and laboratory tests indicate a **useful life approximately five times that of ordinary stoppers.**

The semi-solid stopper is recessed and offers the advantage of greater depth of seal, eliminates popping out, facilitates removal, reduces time required for special boring and requires less rubber than the usual solid stopper. The recess also forms a well for lubricants when using a cork borer.

In the one and two-hole stoppers, the usual cylindrical bore is replaced by fusiform openings with funnel tops. They offer the advantage that tubing can be inserted more readily and with less danger of personal injury than in the usual openings—particularly by students. They also permit the insertion of larger tubes than is possible with the usual openings.

Available in sizes 00 to 15, inclusive. Current prices and more detailed information sent upon request.

*Subject to requirements of NPA Reg. M-2, "Rubber".

ARTHUR H. THOMAS COMPANY

LABORATORY APPARATUS AND REAGENTS

WEST WASHINGTON SQUARE
PHILADELPHIA 5, PA.
Teletype Services: Western Union WUX and Bell System PH-72

JOURNAL OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVII MAY 1952 No. 5

DEAN WILLIAMS ..... *Editor*

EDITORIAL BOARD

H. B. MERRILL R. B. HOBBS F. O'FLAHERTY
R. E. PORTER J. H. HIGHBERGER H. G. TURLEY

Only such correspondence as pertains to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Correspondence in reference to subscriptions, advertising and other business should be addressed to the Secretary, Dept. of Leather Research, University of Cincinnati, Cincinnati 21, Ohio.

Checks for subscriptions and advertisements should be made payable to the American Leather Chemists Association.

Subscriptions—Members, $12.00 annually; Non-members, $15.00 annually.

Published monthly by the American Leather Chemists Association

Entered as Second-class Matter at the Post Office at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

Copyright, 1952, by the American Leather Chemists Association.

PAST PRESIDENTS OF THE A. L. C. A.

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VETCH, W. K. ALSOP, L. E. LEVI, C. R. OBERFELL, R. W. GRIFFITH, C. C. SMOOT, III, J. S. ROGERS, LLOYD BALDERSTON, J. A. WILSON, R. W. FREY, G. D. McLAUGHLIN, FRED O'FLAHERTY, A. C. ORTHMANN, H. B. MERRILL, V. J. MLEJNEK, J. H. HIGHBERGER, DEAN WILLIAMS, T. F. OBERLANDER, A. H. WINHEIM.

OFFICERS 1950-'51

President—R. M. Koppenhoefer, Socony-Vacuum Laboratories, 412 Greenpoint Ave., Brooklyn 22, N. Y.

President-Elect—H. G. Turley, 501 Camden Ave., Moorestown, N. J.

Secretary-Treasurer—Fred O'Flaherty, Department of Leather Research, University of Cincinnati, Cincinnati 21, Ohio.

Council

Robt. B. Hobbs, Leather Division, National Bureau of Standards, Washington, D. C.

C. G. Telander, Armour & Co., Research and Development Dept., Leather Section, 500 Arch St., Williamsport, Pa.

A. W. Goetz, School of Leather & Tanning Technology, Pratt Institute, Brooklyn 5, New York.

W. Windus, 612 Warwick Road, Haddonfield, N. J.

C. M. Morrison, Jr., Reilly-Whiteman-Walton Co., Conshohocken. Pa.

FRANCIS R. MOSBAUGH

It is with deep regret we chronicle the death of Francis R. Mosbaugh, who for more than half a century was prominently identified with the leather industry of the United States and Canada.

Mr. Mosbaugh's eminently successful career began in the mid-nineties in the laboratory of W. W. Mooney and Sons, of Columbus, Indiana, of which city he was a native. Here he acquired a practical as well as a theoretical knowledge of leather manufacture, and later extended this knowledge and the knowledge of tanning materials and extract manufacture with the Acme Bark Extract Company, Damascus, Virginia, and John H. Heald & Company, of Lynchburg, Virginia.

In 1903 Mr. Mosbaugh became associated with the Anglo-Canadian Leather Company, of Huntsville, Ontario, as chemist and technical director, later becoming a member of the board of directors; both of which offices he held until his demise.

He was a co-founder of the A. L. C. A., and in its swaddling years rendered valuable aid in developing the provisional methods of analysis required for a foundation on which to build future advancement. His interest in the progress and growth of the Association never flagged, and at one time he served on the Council.

Mr. Mosbaugh's career was unique, inasmuch as his experience covered practically the entire history of leather chemistry and technology in America from what he termed the "covered wagon days of leather chemistry" until the present.

Possessed of a fine mind, one of his outstanding attributes was his sound thinking on almost any subject, and a day spent in his company never failed to be redundant in knowledge gained and entertainment. Those honored with his friendship could count themselves honored indeed.

Mr. Mosbaugh's interest, as one would expect from one of his indomitable activity, varied from outdoor sports to service on behalf of his community. He was a member of the first Memorial Parks Commission, also a member of the Board of Education and Victoria Order of Nurses. Outdoors he was devoted to golfing, tennis, skiing, etc. As a golfer he was President of the Huntsville Golf Club, to say nothing of being an ardent follower of the gentle art of Isaac Walton.

In 1910 Mr. Mosbaugh was married to Miss Laura Clairmont of Gravenhurst, who survives him together with two daughters and two sons. His church affiliations were in St. Mary's R. C.

In closing this tribute to a friend, gentleman and scholar, may the writer be permitted to say that in the course of a long life he has never known nor heard of a happier or more successful career in both business and personal life than that of Francis R. Mosbaugh. To him, Vale!

GEORGE KERR

WILLIAM S. CALCOTT

William S. Calcott, assistant to the director of the technical section of the DuPont Company's Organic Chemicals Department, died February 15. A number of important DuPont developments were attributed to him. He collaborated with Thomas Midgely and Charles Kettering in the development of a process for the manufacture of tetraethyl lead. In addition to his membership on the Advisory Council for Science and Engineering at the University of Notre Dame, he served on the Chemistry Advisory Committee of Rutgers University. He became a member of our Association in 1949.

H. WEBSTER THOMAS

H. Webster Thomas, an active member of the Association since 1934, died on March 6th while on a business trip for his Company. He had been associated with Rohm and Haas since 1927. Community affairs always held his interest as attested by the numerous local bodies he served in his home of Lexington, Mass. He will be sorely missed by all who knew him.

MINUTES OF MEETING OF THE SUPERVISORY COMMITTEE ON TANNIN ANALYSIS

A meeting of the Tannin Analysis Supervisory Committee was held at the Eastern Regional Research Laboratory, Philadelphia, Pennsylvania on November 8, 1951. The meeting was called to order by Chairman G. W. Stanberry at 10:30 A.M. The following members and guests were present: C. A. Blair, I. D. Clarke, J. H. Davis, G. V. Downing, A. N. Kay, F. P. Luvisi, F. F. Marshall, R. L. Moore, J. S. Rogers, L. Sheard, and J. F. Wagoner.

The minutes of the last meeting held at Groton, Connecticut on June 10, 1951 were approved as published in the October Journal.

The purpose of this meeting was to discuss ways in which the variables encountered between laboratories in a tannin analysis could be minimized or eliminated, and to agree upon needed revisions, refinements and additional details in the text of the methods. Mr. A. N. Kay, who is the Association's representative on the International Commission on Quantitative Tannin Analysis, was selected to rewrite the Methods incorporating the proposals agreed upon. There then followed a lively and lengthy discussion on the details of the methods which resulted in numerous constructive suggestions. One matter that received considerable attention was the moisture loss entailed in the grinding of solid extracts. A Sub-committee to be headed by Mr. J. S. Rogers was formed to investigate this matter. Other members

making up the sub-committee are C. A. Blair, J. H. Davis, G. V. Downing, R. L. Moore, and J. F. Wagoner. The latter agreed to furnish the necessary samples.

Mr. Kay is to draw up a preliminary draft of the methods incorporating the agreed upon changes and submit these to the members for final approval.

The meeting adjourned at 4:30 P.M.

J. F. Wagoner, *Acting Secretary.*

COUNCIL MEETING MINUTES
AMERICAN LEATHER CHEMISTS ASSOCIATION

February 27, 1952
Hotel Statler
New York, New York

The meeting convened at 10:00 A.M. All Officers and Council Members were present except Mr. Arthur Goetz. Also present were Messrs. John Teas, Craig Blair, Dean Williams and J. S. Kirk.

The minutes of the meeting of November 8th were read and received final approval.

Mr. Morrison reported briefly on the organization of his committee to aid the Tanners' Council in their promotion plans. Mr. Morrison has had conferences with Mr. Glass. Dr. Koppenhoefer advised that all future activities will funtion through the committee.

Mr. Teas reported for the Ways & Means Committee. The Secretary furnished copies of the annual statement and a proposed budget.

The balance sheet and statement of income and expense for 1951, which will be published, showed a net surplus for 1951 of $5,043.10. This was due to increased income over reduction in operating costs and to a decrease in Journal printing below the budgeted amount.

The proposed budget for 1952 was discussed and approved by Council. A budget of $27,700.00, as compared to $26,075.00 for 1951, was approved.

Editor Williams reported that he has an unofficial assistant editor in the person of Mr. Ralph H. Twining.

Mr. Blair, Chairman of the Nominating Committee, reported that Mr. Thayer was withdrawing from candidacy of President-Elect. Council asked the Nominating Committee to designate another candidate.

A letter from Mr. Marshall was read and his proposal of a plan for the transfer of the Hide-Powder Business, to the A.L.C.A., was accepted in principle. Dr. Turley was appointed a committee of one to have proper legal instrument prepared.

Council authorized the Secretary to invest $5,000.00 in U. S. bonds from the operating funds on hand.

Council approved a charge of $8.00 per 1/4 page space in the Directory.

Council also approved a plan for the 1953 Directory which is to list with each persons name, the firm affiliation as well as the home address.

A committee is to be appointed by the President to study the advisability of including in some future Directory some biographical data on each member.

Dr. Turley reported on the technical committees.

Council approved the publication of a new issue of Methods Booklets as soon as Dr. Turley can assemble the material. When such Methods Booklets are available, they are to be sold at cost.

Mr. Thayer resigned as chairman of the Convention Committee and Dr. J. S. Kirk was appointed chairman. Dr. Kirk was present and reported briefly on the Annual Meeting.

Council approved the wording of the Award Committee's plan for the Winheim Award as published in the minutes of the meeting of November 8th.

A list of the members resigning was read and accepted.

The following members were elected to active membership -

Mr. Werner R. Busche
Mr. Enrique Uribe
Mr. Eugene Dogliotti

Council approved the change in name of the "Stream Pollution Sub-Committee" to the "Industry Waste Disposal Committee" with no change in personal.

The meeting was adjourned at 4 P.M.

Respectfully submitted,

FRED O'FLAHERTY, *Secretary*.

EXHIBIT "A"

COMPARATIVE BALANCE SHEET

DECEMBER 31, 1951 and DECEMBER 31, 1950

ASSETS

	1951	1950	Increase or (Decrease)
CASH			
Petty Cash	$ 6.84	$ 13.55	$ *6.71*
Cash in Bank	14,470.08	9,637.54	4,832.54
RECEIVABLES			
Accrued Interest Receivable on U. S. Treasury Bonds	62.50	62.50	——
Accounts Receivable Advertisers	2,074.61	1,743.25	331.36
Accounts Receivable—Reprints	263.70	——	263.70
INVESTMENTS			
United States War Bonds Series "F" cost $5,920.00 plus accrued interest of $1,356.00 to December 31, 1951	7,276.00	7,056.00	220.00

United States Treasury Bonds–2½% due for redemption in 1972 but redeemable on and after June 15, 1967—cost	13,000.00	13,000.00	——
United States Treasury Bonds—2½% Series, "G" due July of 1958 at cost	5,000.00	5,000.00	——
United States Treasury Bonds Series "F" cost $3,700.00 plus accrued interest earned of $100.00 to December 31, 1951. Due in November 1960 at par	3,800.00	3,745.00	55.00
TOTAL ASSETS	$45,953.73	$40,257.84	$ 5,695.89
LIABILITIES			
CURRENT LIABILITIES			
Accounts Payable	$ 1,158.44	$ 1,415.92	$ *257.48*
Accrued Withholding Tax Liability	94.20	79.20	15.00
DEFERRED CREDITS TO INCOME			
Advertising paid in advance		20.00	*20.00*
Dues received in advance	376.35	268.10	108.25
Subscriptions received in advance	2,055.91	1,248.89	807.02
TOTAL LIABILITIES	$ 3,684.90	$ 3,032.11	$ 652.79
NET WORTH			
SURPLUS			
Surplus as per Exhibit "C"	$42,268.83	$37,225.73	$ 5,043.10
Total Net Worth	42,268.83	37,225.73	5,043.10
TOTAL LIABILITIES AND NET WORTH	$45,953.73	$40,257.84	$ 5,695.89

EXHIBIT "B"

COMPARATIVE STATEMENT OF INCOME AND EXPENSE

YEARS ENDING DECEMBER 31, 1951 and DECEMBER 31, 1950

	Years Ended December 31, 1951	1950	Increase or (*Decrease*)
INCOME			
GENERAL			
Dues (including members' subscriptions to Journal (Net)	$ 8,827.53	$ 8,703.75	$ 123.78
By-Laws and Methods	117.90	175.60	*57.70*
Membership Booklets (Directory)	495.49	460.20	35.29
Interest on Government Bonds	725.00	653.00	72.00
Totals	$10,165.92	$ 9,992.55	$ 173.37
JOURNAL (Exclusive of Members' Subscriptions)			
Advertising	$10,319.32	$10,358.90	$ *39.58*
Subscription (Non Members)	4,112.06	3,775.00	337.06
Journals Bound and Unbound	1,310.38	988.85	321.53
Reprints	2,032.00	1,360.74	671.26
Dues S.L.T.C.	643.25	614.45	28.80
Totals	$18,417.01	$17,097.94	$ 1,319.07
TOTAL INCOME	$28,582.93	$27,090.49	$ 1,492.44
EXPENSES			
GENERAL			
Salary of Secretary	$ 3,569.59	$ 3,433.28	$ 136.31
Office Expenses, Stationery, Postage, Telephone, etc.	794.92	1,188.84	*393.92*
Accounts Receivable Written Off—Uncollectible	255.00	275.00	*20.00*

Annual Meeting Expense	——	5.08	*5.08*
Auditing	100.00	100.00	——
Association Emblems	*13.50*	286.43	*299.93*
By-Laws and Methods	130.00	——	130.00
Council Meeting Expense	176.17	63.44	112.73
Dues, International Leather	117.60	117.60	——
Membership Booklets (Directory)	521.50	501.25	20.25
President's Letter	——	73.31	*73.31*
President's Expense (ACS Meeting)	69.22	——	69.22
Winheim Memorial Award	100.00	——	100.00
Totals	$ 5,820.50	$ 6,044.23	*223.73*
JOURNAL			
Journals	$13,741.94	$15,333.34	$ *1,591.40*
Editor's Compensation	900.00	900.00	——
Editor's Expense	502.92	555.40	*52.48*
Insurance Expense (Old Journals)	58.00	58.00	——
Miscellaneous Journal Expense, Counting, Binding, Postage, etc.	137.41	33.45	103.96
Registered Copyrights	48.00	48.00	——
Reprints	1,751.85	2,320.15	*568.30*
Storage	350.00	350.00	——
Exchange on Foreign Checks	3.76	2.62	1.14
Translations and Abstracts	208.77	273.84	*65.07*
Committee Work	16.68	432.33	*415.65*
Totals	$17,719.33	$20,307.13	$ *2,587.80*
TOTAL EXPENSE	$23,539.83	$26,351.36	$ *2,811.53*

EXHIBIT "C"

COMPARATIVE STATEMENT OF SURPLUS

	Years Ended December 31 1951	1950	Increase or *(Decrease)*
Surplus at the beginning of the year	$37,225.73	$36,486.60	$ 739.13
Add			
NET PROFIT			
General (Including members' subscriptions to Journal)	4,345.42	3,948.32	397.10
Journal (Exclusive of members' subscriptions to Journal)	697.68	3,209.19**	3,906.87
SURPLUS AT THE END OF THE YEAR	$42,268.83	$37,225.73	$ 5,043.10

**Difference between Journal Income and Journal Expense of 1950 which resulted in a loss.

Effects of Tannery Processes on the Electronoscopic Appearance of Bovine Hide Collagen Fibrils*

R. Borasky† and J. S. Rogers

*Eastern Regional Research Laboratory***
Philadelphia 18, Pennsylvania

Introduction

Leather manufacture may be defined as a series of processes by which the collagen of skin is converted into leather. In recent years, it has been shown that the collagen fibril is a fundamental structural unit of collagenous tissue [1, 2]. This unit is so small it can be observed directly only in the electron microscope.

Occasional references to the electronoscopic appearance of tanned collagen fibrils, and of collagen treated with some reagents commonly used in the tanning industry, may be found in the literature [3, 4, 5, 6, 7]. However, no investigation has been reported that was specifically designed to determine the effects of those reagents commonly used in beamhouse and tanning operations on the electronoscopic appearance of collagen fibrils. Observations and results of such an investigation will be presented in this paper.

Experimental

With one or two exceptions, the collagen used was derived from fresh bovine corium cubes. The corium cubes were dispersed in a Waring Blender, and the collagen fibrils were isolated by repeated suspension and centrifuging. Dispersions so prepared contained from 10 to 100 milligrams of collagen fibrils per 100 milliliters of dispersion.

Twenty-five milliliter portions of the collagen dispersion were used for each treatment. For brine curing, liming, pickling, and chrome tanning, the dispersions were put in dialysis bags and suspended in 10 volumes of the treatment liquors. For bating and tanning with tan liquors other than chrome, the dispersions were mixed with an equal volume of the treatment solutions. The concentration of reagent in each treatment liquor was adjusted so that an excess of the reagent was assured.

Shrinkage temperature values, determined by the microscopic method [8], were used as an index of tanning.

Samples of the collagen dispersions were prepared for electronoscopic examination before and after each treatment. Specimens were usually examined and photographed at a magnification of about 11,000 diameters.

*Presented at the 47th Annual Meeting of the American Leather Chemists Association, Groton, Connecticut, June 12, 1951.

**One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

† Present address: General Electric Company, Richland, Washington

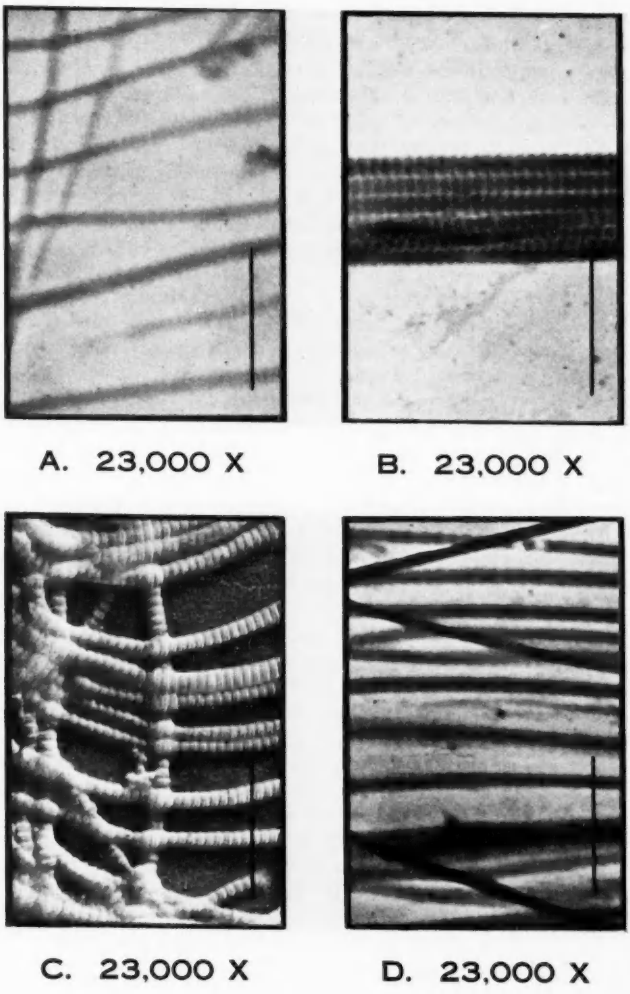


FIGURE I. BOVINE HIDE COLLAGEN FIBRILS.
A. Untreated. Dried on specimen grid.
B. Untreated. Stained with 1% P.T.A.
C. Untreated. Shadowed with chromium.
D. Untreated. Fixed with osmic acid. Dried by Anderson technique.

Results and Discussion

The collagen fibrils used in this investigation were of colloidal dimensions and were unprotected by association with other fibrils or with other skin constituents, such as elastin. Therefore, the collagen was many times more reactive than the collagen of intact skin. For this reason, the effects of reagents such as acids, alkalies and enzymes may be exaggerated, because the reaction of the collagen with the reagent proceeds at a faster rate or goes further than that with undispersed hide. This factor and the inherent limitations of electron microscopy [3—6], were constantly borne in mind, and due allowances were made for them in interpreting the observations and results.

"*Native*" *or Untreated Collagen*

The first series of electron micrographs (Figure I) illustrates the characteristic properties of native or untreated collagen fibrils. These micrographs also represent fibrils cured by drying in air.

Figure I shows four representative micrographs of untreated or "native" bovine hide collagen fibrils. The vertical line in the lower right-hand corner of each micrograph represents 1 micron, or 1/25,000 of an inch. The fibrils in Figures I A, I B, and I C, in general, are wider than the fibrils in Figure I D. In all instances, the fibrils are infinitely long, as compared with their width. The collagen in Figure I A has low electron scattering power, and the characteristic periodic striations are just barely discernible. Axial periodicity is distinct in the fibrils of Figure I B. The average length of the axial period is 650 Å. Note the sub-period bands. The shrinkage temperature (Ts) of the phosphotungstic acid (P.T.A.) stained collagen was 60°C., as compared with 63°C. for untreated collagen. This indicates that P.T.A.-stained collagen is not tanned. The chromium-shadowed collagen in Figure I C has the same over-all dimensions as the fibrils in Figures I A and I B. The width-to-height ratio of the fibrils in this preparation is approximately 2.75:1. The hills and valleys (bright and dark bands) in the fibrils correspond to the dark and light bands of the previous pictures.

It is of special interest to note how the fibrils flatten where they cross one another. When biological materials are dried in air or in the evaporator previous to shadowing, they are subjected to great surface tension forces, which flatten the specimens and press them into the supporting film [9]. This makes for poor definition of the specimen edges and sometimes distorted images. The drying technique devised by Dr. T. F. Anderson eliminates surface tension forces by the use of liquid CO_2 at the critical temperature and pressure [9]. Figure I D shows cowhide collagen dried by the Anderson technique*. Compared with the fibrils in Figure I A, these fibrils have noticeably greater electron scattering power. The increased electron scattering power is ascribed to the osmic acid fixation and also to the fact that these

*The authors are indebted to Dr. T. F. Anderson, of the Johnson Foundation, University of Pennsylvania, for preparing the specimens.

fibrils are more nearly round than the fibrils in Figures I A, I B, and I C. This view is supported by the fact that the average width of these fibrils is less than the average width of fibrils dried by the usual methods.

Only dry fibrils can be observed in the electron microscope. From their electronoscopic appearance, however, it is possible to gain some knowledge concerning the state of hydration of the fibrils before drying. By replica techniques, Gross has shown that the edges of moist fibrils are smooth, whereas the edges of dried fibrils are serrated [10]. The fibrils in Figures I A, and I B have the appearance of hydrated fibrils because their edges are smooth. In shadowed preparations, such as shown in Figure I C, collagen fibrils invariably have serrated edges. Serrated or beaded fibril edges are frequently found in preparations not shadowed, but they are by no means characteristic [3, 4]. The higher electron scattering portions of the collagen fibril may represent loci of slightly higher concentration of protein, or high concentrations of positively charged water-binding end groups such as free amino groups of lysine [11]. In shadowed preparations, the high scattering portions are thicker than the low scattering portions of the fibrils. The low scattering parts of the fibrils (light bands of stained fibrils or valleys of shadowed fibrils) may represent loci of slightly lower protein concentration. This evidence suggests that the serrated fibril edges are formed on drying by the loss of water from low electron-scattering portions (the light bands).

Briefly, "native" or untreated collagen fibrils are smooth cylinders that are infinitely long as compared with their diameters. The fibrils are plastic and tend to flatten when dried by ordinary methods. The edges become serrated because of loss of water from the low electron-scattering portions of the fibril. Collagen fibrils have characteristic periodic striations, the average length of the period being 650 Å.

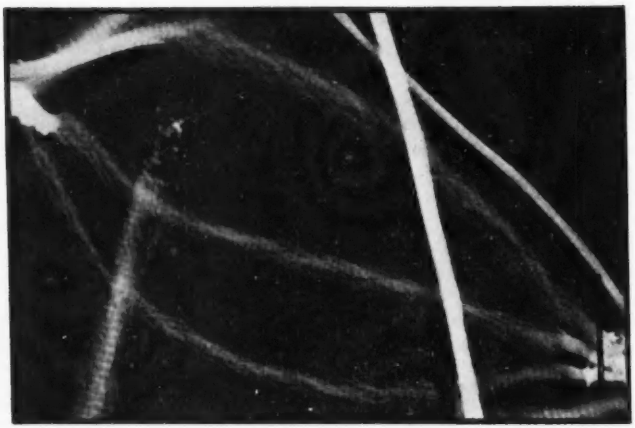
Effects of Curing and Beamhouse Processes

In general, curing and beamhouse operations preserve, purify and prepare the collagen of skin for the reaction with tanning agents. These processes, if properly conducted, should not produce any permanent deleterious effects on the collagen. The electronoscopic appearance of collagen fibrils treated with saturated salt (NaCl) solutions is identical with that of untreated native, or fresh, collagen fibrils. Similarly, limed, bated, or pickled collagen fibrils present the normal electronoscopic appearance when the treatment reagent is completely removed. However, if the collagen fibrils are derived from improperly cured hides, if liming and bating are unduly prolonged, or if the pickle liquor does not contain enough salt, there are marked changes in the electronoscopic appearance of the collagen fibrils.

Figure II A shows cowhide collagen which was soaked in a 0.4 per cent acetic acid solution (pH 3.5) overnight. The collagen was stained with P.T.A. to enhance periodic structure. The shrinkage temperature (Ts) of this collagen was less than 40°C.

A. 12,500 X

B. 19,000 X



C. 19,000 X

FIGURE II. FILAMENTED BOVINE HIDE COLLAGEN FIBRILS.

A. Treated with 0.4% acetic acid; pH 3.5. Stained with P.T.A.
B. Obtained from improperly cured cowhide; pH 5.5. Shadowed with palladium.
C. Treated with sodium silicofluoride; pH 3.3. Shadowed with uranium.

Figure II B is a palladium-shadowed preparation of collagen fibrils obtained from a salt-cured cowhide which had been stored in a damp, cold room for more than 6 months. The Ts of this collagen was 55°C. The pH of the collagen dispersion was 5.5. Figure II C is a uranium-shadowed preparation of collagen which was soaked in a saturated (0.3%) solution of sodium silicofluoride. The pH of the solution was 3.3, and the Ts of the collagen was 46-47°C.

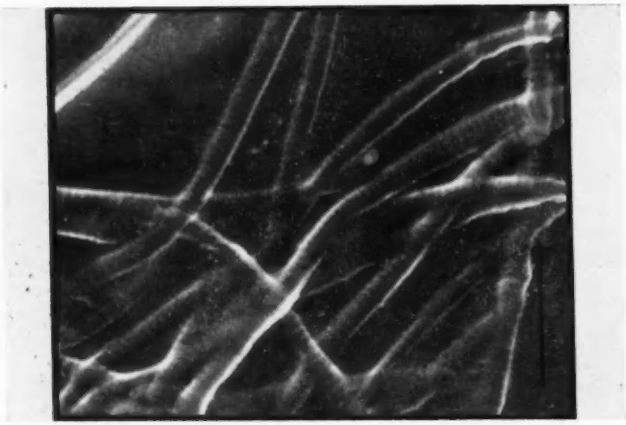
The splitting of collagen fibrils into their component filaments as shown in Figure II may be regarded as the first stage in the degradation of collagen. Filamentation results from prolonged soaking in water, as shown in Figure II B; by soaking in solutions with high hydrogen ion concentrations, as shown in Figures II A and II C; by soaking in highly alkaline solutions [1,2] (Figure III B); and by soaking in solutions of certain salts such as $BaCl_2$ [3]. In all these instances, adequate concentration of sodium chloride prevented longitudinal splitting into filaments. Thus collagen soaked in a saturated NaCl brine for months had the same electronoscopic appearance and shrinkage temperature as fresh collagen. The same was true of collagen soaked in a pickle liquor (10 per cent NaCl solution adjusted to pH 2.0 with HCl) or in a saturated sodium silicofluoride solution containing 10 per cent NaCl (pH 3.3).

From these observations, we may conclude that sodium chloride is effective in preventing collagen fibrils from splitting into their component filaments. Collagen fibrils derived from properly cured and stored hides rarely are filamented. The collagen shown in Figure II B came from a salt-cured hide from which some of the salt was leached out during storage in the damp, cold room. Consequently, the concentration of salt was not high enough to prevent the onset of degradation, as evidenced by the filamentation. This type of degradation (filamentation) may also take place in soaking-back operations. As will be shown later, the collagen is digested by enzymes only after the fibrils are filamented. These results are in accordance with the results obtained in practice when salt is added to the soak liquors for dried skins, which usually require long soaking periods.

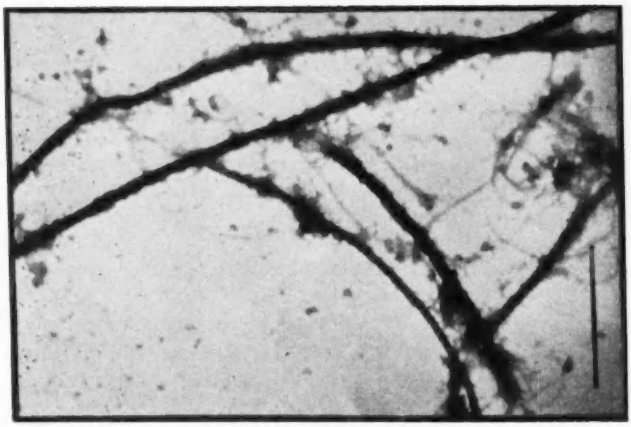
Sodium silicofluoride is added to curing salt to function as a rodenticide, insecticide and mothproofing agent. Used alone, sodium silicofluoride damages the collagen. This is the effect of the pH [8]. When used in conjunction with sodium chloride, it does not affect the collagen and affords the cured hides protection against damage by rodents, insects and moths.

Acid is used in pickle liquors to adjust the pH of the collagen so that it will be compatible with the acid pH of the chrome-tan liquors. Acid alone causes considerable damage, as shown in Figure II A, but when used with sufficient salt it does not affect the collagen.

Briefly, sodium chloride prevents collagen filamentation, but does not interfere with the functioning of other reagents, such as acids in pickle



A. 23,000 X



B. 23,000 X

FIGURE III. LIMED BOVINE HIDE COLLAGEN FIBRILS.

A. Limed for 1 hour. pH of washed dispersion, 10.5. Shadowed with chromium.
B. Limed for 24 hours. pH of washed dispersion, 6.5. Stained with P.T.A.

liquors, or pesticides, such as sodium silicofluoride, in curing mixtures or brines.

Figure III A shows a chromium-shadowed preparation of collagen, which was treated with a saturated lime solution for 1 hour. The dispersion was washed by dialysis but was not completely free of lime, as shown by the fact that the washed disperions had a pH of 10.5. Many individual fibrils vary in width. They are flattened, as evidenced by the relatively short shadow. Their fibril edges are smoother, and the periodic structure is less pronounced than in the fibrils of Figure I C. These characteristics indicate that the fibrils were in a thoroughly hydrated form before they were prepared for electron microscopic observation. If the lime is completely removed, as shown by a dispersion pH of 5.5 to 6.0, the fibrils have the appearance of normal untreated fibrils in every respect.

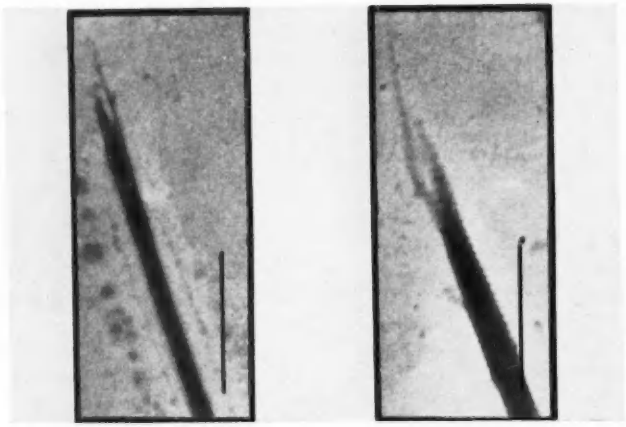
Figure III B shows collagen which was treated with saturated lime solution for 24 hours. The lime was completely removed by dialysis against water. The pH of the washed dispersion was 6.5. This preparation was stained with P.T.A. Small tufts of filaments along the edges give the fibrils a frayed, ravelled appearance. The fibril ends are frayed. Numerous collagen filaments may be seen in the background. Several are of finite length. Fibrils of finite length, which are invariably found in preparations of degraded collagen, are a good indication of irretrievable damage. The periodic structure is obscured by excess stain. This micrograph of limed collagen was selected because it shows degradation due to excess liming and illustrates a case in which the reaction proceeded at a faster rate than desired. However, it is not typical. We have examined many disperions of collagen limed for 24 hours, whose electronoscopic appearance after washing was identical with that of fresh collagen. (The tanned collagen fibrils shown in Figure V A were limed for 24 hours and bated for 1 hour before tanning.)

From these observations, we conclude that when collagen swells in lime liquor, the swelling is temporary and reversible, in that upon removal of the lime, the collagen recovers its normal appearance. Excess liming, however, caused filamentation and breaking of the collagen fibrils into short lengths, signifying irretrievable collagen degradation.

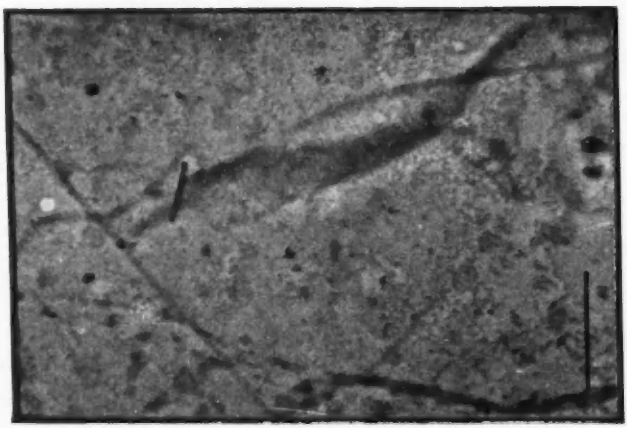
There has been, and still is, much controversy on the effects of bating on hides and skins, especially on the effect of the bates on the collagen. Electron microscope observations suggest that the intact collagen fibril is not subject to enzymatic attack. It is only after the fibril is broken down into filaments or is degraded into soluble products, such as gelatin, that the enzymes can attack the collagen [1,2].

Figure IV A shows collagen treated with Oropon A* for 2½ hours at 37°C. The fibril was stained with P.T.A. Figure IV B shows collagen

*Mention of commercial products does not imply that they are endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.



A. 23,000 X B. 23,500 X



C. 19,000 X

FIGURE IV. ENZYME-TREATED COLLAGEN FIBRILS.

A. Bullhide collagen treated with Oropon A for 2½ hours. Stained with P.T.A.
B. Cowhide collagen treated with papain. Stained with P.T.A.
C. Sharkskin collagen treated with trypsin.

treated with 0.1 per cent papain in acetate buffer (pH 4.8) and activated with 0.01 M cysteine. This preparation was also stained with P.T.A. Figure IV C shows sharkskin collagen, which was digested by trypsin (pH 7.8) at 37°C. for 2 hours.

The fibril in Figure IV A is normal in every respect except the fibril end, which is tapered. The pH of the dispersion was 6.5. Figure IV A is not a typical micrograph. Most of the collagen fibrils from the same preparation had the same appearance and average dimensions as the fibrils shown in Figure I.

Figure IV B shows more clearly the characteristics of the tapered fibril ends of enzyme-treated collagen. The main shaft of this particular fibril is about 0.2 micron wide and tapers down to about 0.04 micron at the tip. The fairly well defined period striations in the shaft measure about 600 Å. The width and shortened spacings indicate that the shaft of the fibril is swollen. The sharkskin collagen in Figure IV C is obviously much degraded. The debris in the background is probably degradation products of the collagen.

The three micrographs in Figure IV illustrate enzymatic-digested collagen fibrils. As pointed out previously, limited exposure to enzymes does not alter the characteristic appearance of collagen fibrils. Enzymatic digestion of collagen may be considered a two-stage process. The first stage is the breakdown of the fibrils into filaments, or into water-soluble products such as gelatin. In this degraded form, the collagen is available to the enzyme for digestion, which is the second phase. The initial breakdown of the fibrils to smaller components or soluble degradation products is caused by one or more factors. As illustrated below, for optimal activity, a particular enzyme requires specific conditions of pH, temperature, and frequently specific activators. When collagen is placed in a medium devoid of enzyme, but adjusted for optimal activity of a specific enzyme, the collagen splits into its component filaments, swells, or is actually degraded into soluble products such as gelatin. Thus for peptic digestion, a pH of 2.0 – 2.5 is required. In media from pH 0.5 – 3.5, collagen fibrils split into their component filaments (Figure II A and II C). Collagen fibrils break up into their component filaments when allowed to stand in phosphate buffers at pH 7.0 or in citrate buffers at pH levels from 4 to 7 for extended periods of time at 30 – 37°C.[2] The start of the shrinking reaction when collagen is gradually heated in water is characterized by swelling and gelatinization of the fibril ends[3]. In each instance noted above, the collagen fibril is broken down into filaments or hydrolyzed to a soluble degradation product.

Sharkskin collagen (Ts 45°C.) is much more easily attacked by trypsin than is cowhide collagen (Ts 63°C.), principally because it is more sensitive to warm water than is the cowhide collagen. A possible explanation for the fact that pepsin digests collagen much more rapidly and more completely than does trypsin is that at pH 2 the collagen fibril is in the form of filaments (Ts below

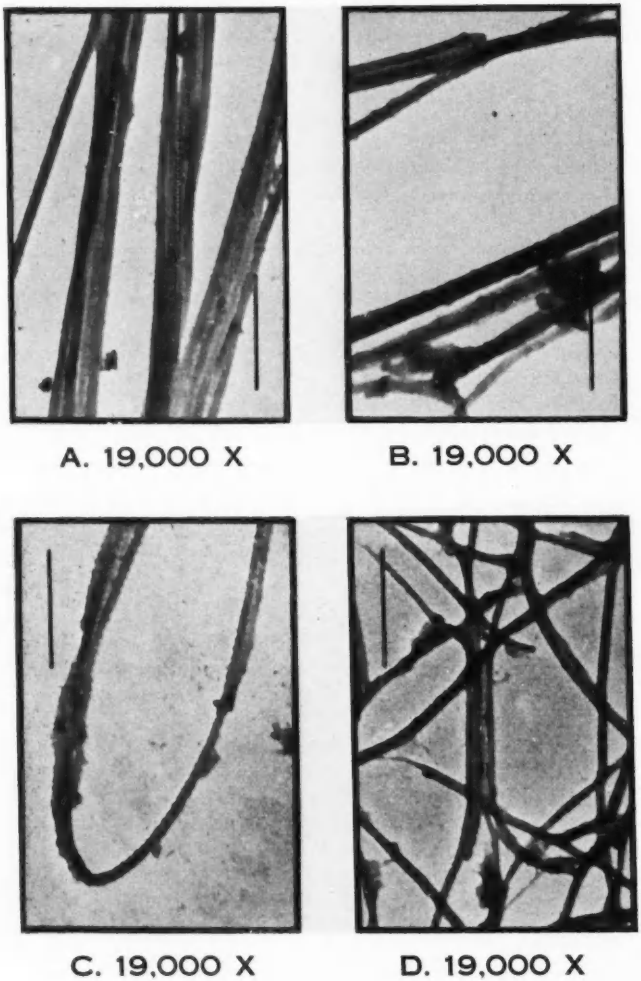


FIGURE V. TANNED BOVINE COLLAGEN FIBRILS.

A. Tanned with a 50–50 blend of chestnut-sulfited quebracho liquor. Ts=89°C.
B. Tanned with Orotan. Ts=86°C.
C. Tanned with canaigre extract. Ts=98°C.
D. Tanned with sumac extract. Ts=80°C. Shadowed with palladium. Positive print.

40°C.), which are much more sensitive to warm water than intact fibrils (Ts about 63°C.) at pH 7.5 – 8. In all instances, the ends are more subject to degradation than the main body of the fibril; thus, the degraded ends are digested by the enzyme and become tapered.

From these observations, we may conclude that bating, if properly conducted in the beamhouse, will not destroy the collagen of skin. Bating solubilizes non-collagenous proteins such as elastin and whatever collagen may have been degraded in prior beamhouse processes. If the bating is allowed to go on for too long a period at the optimum temperature for bating, the collagen is attacked, and there is a definite loss of hide substance.

Effects of Tanning Agents on the Electronoscopic Appearance of Collagen Fibrils.

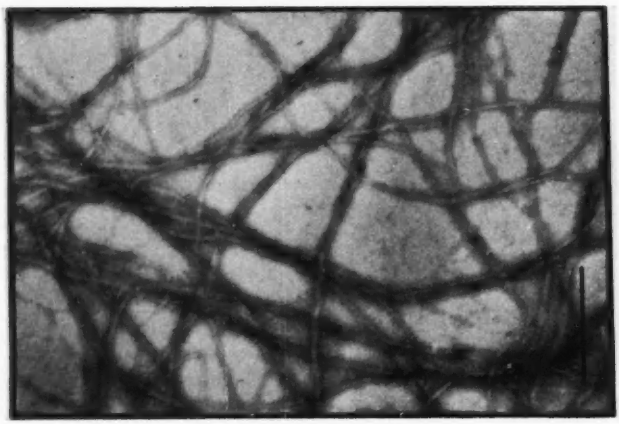
The electronoscopic appearance of tanned collagen fibrils is somewhat different from that of untanned fibrils. These differences will become apparent as we examine and discuss the subsequent electron micrographs. When tan liquor was added to a collagen dispersion, the collagen fibrils aggregated and formed a fibrous clot. After being washed, the fibrous clots were dispersed in water by teasing or in a Waring Blendor.

Figure V A shows collagen tanned with a 50–50 blend of chestnut-sulfited quebracho tan liquor. The Ts of the washed and redispersed vegetable-tanned collagen was 89°C. The fibrils are more nearly round than those of untanned collagen, but not quite so round as fibrils of chrome-tanned collagen (Figure VI B). The fibril edges are comparatively smooth. Period and intra-period structures are obscured. In a few places where the macro periodicity may be measured, the average length per period is within the normal range (600–700 Å). Periodicity is more clearly defined in shadowed preparations (Figure V D). Contrast between the tanned fibrils and the background is better than between untreated fibrils and background (Figure I A). The increase in electron scattering power is ascribed in part to the circular form of the tanned fibrils and in part to the fact that there is more material (collagen plus tannin) to scatter electrons.

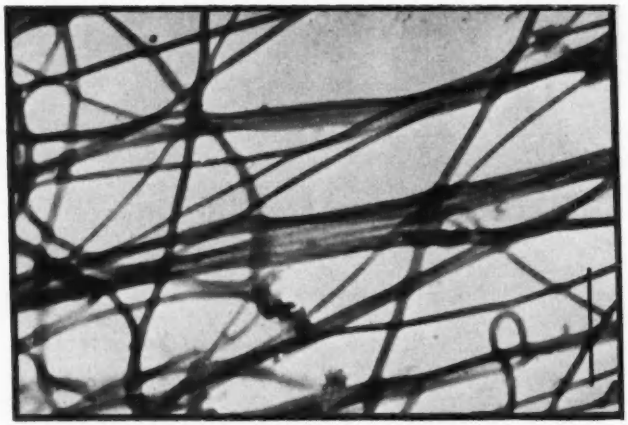
Figure V B shows collagen tanned with Orotan. The Ts of the washed redispersed tanned collagen was 86°C. The contrast of the fibrils against the background is good and, in general, the electronoscopic features are the same as for the chestnut-quebracho tanned fibrils. Figure V C shows canaigre-tanned collagen fibrils. The Ts of this preparation was 98°C. Periodic structure is fairly well defined, more so than in the Orotan-tanned collagen.

Figure V D is a positive print of lightly palladium-shadowed sumac-tanned collagen fibrils. The general dimensions of these fibrils are the same as in Figures V A, V B, and V C, and fine period structure is more or less obscured.

The tendency for the tanned fibrils to aggregate and form small bundles is apparent in all micrographs of tanned collagen (Figure VI B). This



A. 19,000 X



B. 19,000 X

FIGURE VI. CHROME TANNING.

A. In 3% chrome alum liquor, plus 10% NaCl; pH 2.8.

B. The same collagen after neutralization; pH 4.5. Ts 99°C.

aggregation may be due to the formation by the tanning material of the same type of chemical bonds between the fibrils as are formed between the collagen molecules in the fibrils.

Figure I A shows that where two collagen fibrils cross, the electron-scattering power is not materially increased. In Figure I C, the fibrils are flattened where they cross. These observations denote an elliptical cross section and a fair degree of plasticity in untreated collagen fibrils. In tanned collagen fibrils, points at which fibrils cross show a marked increase in electron-scattering power and little tendency to flatten, signifying that the tanned fibrils are more nearly circular and less plastic.

Figure VI A shows collagen fibrils from a dispersion suspended in a chrome-alum liquor (pH 2.8) to which 10 per cent sodium chloride was added to prevent swelling. The salt was added a few minutes after the dispersion was suspended in the chrome liquor. Figure VI B shows the same collagen after the pH of the liquor was adjusted to 4.5 with sodium bicarbonate solution. The collagen in Figure VI A appears to be tubular. This illusion is created by the fact that there is excess chromium along the edges of the fibrils and the fibrils appear to be devoid of periodicity. Close inspection of the original prints, however, reveals fine cross-banding in limited portions of many of the fibrils.

The chromium does not seem to have penetrated into the fibrils at this pH. Similar observations were obtained when properly reduced commercial chrome tan liquors were used instead of the 3 per cent potassium chrome alum liquor. The chrome-tanned collagen fibrils shown in Figure VI B have the same features outlined for the vegetable- and syntan-tanned fibrils shown in Figure V.

TABLE I

Some Physical and Electronoscopic Properties of Collagen Fibrils

Property	Untanned	Tanned	
		Chestnut-Quebracho	Chrome Alum
Shrinkage temperature	63°C.	89°C.	99°C.
Reaggregation of dispersed fibrils	Very little, if any	Pronounced	Pronounced
Electron scattering power (contrast)	Poor	Good	Good
Shape of cross section	Pronounced ellipse	Slightly elliptical	Circular
Plasticity (flattening of fibrils where they cross each other)	Pronounced	Slight	Slight
Period structure	Fairly distinct	Mostly obscured	Mostly obscured

Table I shows some physical properties and the electronoscopic features of untanned (Figure I A), vegetable-tanned (Figure V A), and chrome-tanned (Figure VI B) collagen fibrils.

Summary and Conclusions

The effects of pretanning and tanning processes on collagen fibrils were studied by examining the fibrils in the electron microscope before and after treatment.

The fundamental fibrous units of skin collagen are so small they can be seen only in the electron microscope. The fibrils are smooth cylinders, which are infinitely long as compared with their diameters. The fibrils are plastic and when dried have an elliptical cross section.

The initial stage of collagen degradation is the longitudinal splitting of collagen fibrils into their component filaments. This filamentation occurs when collagen fibrils are allowed to soak in water for prolonged periods of time, or when soaked in a highly acid or highly alkaline medium or in solutions of salts such as $BaCl_2$.

Adequate concentrations of sodium chloride in green salted skins, in curing mixtures and in pickle liquors prevent collagen fibril filamentation.

The swelling of collagen fibrils in lime liquors is reversible. Excess liming causes irreversible collagen degradation.

Bating is an enzymatic digestion of the non-collagenous proteins and of the degraded collagen left in skin after curing and liming. The enzymatic digestion of collagen is a two-stage process. The initial stage, the degradation of the collagen into filaments or water-soluble products, is produced by environmental conditions (pH, temperature, specific activators) essential for optimal enzyme activity. The second stage is the digestion of the degraded collagen by the enzyme. Prolonged bating causes a loss in hide substance.

In general, pretanning or beamhouse processes do not alter the characteristic appearance of collagen fibrils.

Collagen may be degraded when salt cured skins are stored under highly humid conditions, which results in reducing the salt content to less than that required, when skins are subjected to prolonged soaking in lime liquors or prolonged bating, or when there is an inadequate concentration of salt in pickle liquors.

Tanned collagen fibrils are different from untanned fibrils in the following respects. Tanned fibrils have higher shrinkage temperatures. Tanned fibrils tend to appear as aggregates rather than separate individual fibrils. They have good electron-scattering power. The cross section of dried tanned fibrils is more nearly round than that of untanned fibrils. They are less plastic then untanned fibrils.

This electron microscope study of collagen at different processing stages from fresh hide or skin to tanned leather provides a better understanding of

the effects of the various processing treatments. The illustrations make it possible to visualize more clearly the changes that take place in the fibrils during processing and indicate some extreme treatments which might result in degradation of the collagen fibrils.

References

1. Wasserman, F., Anatomical Record, 109, 410 (1951).
2. Borasky, R., Unpublished Results.
3. Nutting, G. C., and Borasky, R., *J. Amer. Leather Chem. Assoc.*, **43**, 96 (1948).
4. Schmitt, F. O., *J. Amer. Leather Chemists Assoc.*, **39**, 430 (1944).
5. Schmitt, F. O., and Gross, J., *J. Amer. Leather Chemists Assoc.*, **43**, 658 (1948).
6. Wolpers, C., *Das Leder*, **1**, 3 (1950).
7. Zaides, A. L., and Pupko, S. L., *Doklady Akad Nauk* S.S.S.R., **73**, 991 (1950); ibid, *Kolloid, Zhur*, **12**, 275 (1950).
8. Borasky, R., and Nutting, G. C., *J. Amer. Leather Chemists Assoc.*, **44**, 830 (1949).
9. Anderson, T. F., *J. Applied Physics*, **21**, 724 (1950).
10. Gross, J., and Schmitt, F. O., *J. Expt. Med.*, **88**, 555 (1948).
11. Mellon, E. F., Korn, A. H., and Hoover, S. R., *J. Am. Chem. Soc.*, **69**, 827 (1947).
12. Borasky, R., Doctoral Dissertation, Georgetown University, Washington, D. C. (1950)

Received Jan. 27, 1952.

Discussion

J. H. Highberger: The electron miscroscopic results of collagen research of the last few years have yielded a characteristic picture of collagen fibrils which Dr. Borasky has described to you this morning. I think the most characteristic thing about this picture is the repetition of the period of 640 to 650 Angstom units which Dr. Borasky mentioned, which might be spoken of as the molecular fingerprint of collagen. This characteristic fine structure has enabled the ready identification of collagen fibrils by the electron microscope, in the presence of other types of fibrous materials.

In regard to the effects of tannery processes, Dr. Borasky's electron micrographs would appear to indicate that these, with the exception of drastic liming, produce no marked effect on this characteristic fine structure picture of collagen. I might say that the fragmentary results which we have obtained in our own laboratories would tend to confirm this.

I should like to mention the following fact which, of course, Dr. Borasky is quite aware of, for the information of those who are not familiar with electron miscroscopic techniques. One has to be extremely cautious in the interpretation of the results obtained, because of the fact that one deals with extremely minute samples of material. One must be quite certain, through repeated observation and by other means, that what one sees is really representative of the whole. I do not mean this to be any criticism of what Dr. Borasky has described and has shown. I merely present it for the information of those who are not familiar with the field.

I have mentioned the characteristic electron miscroscopic appearance of collagen fibrils and I thought it would be appropriate in connection with the discussion of Dr. Borasky's paper to draw your attention to some very recent results connected with the fine structure of collagen which my associates, Dr. Schmitt and Dr. Gross, of the Massachusetts Institute of Technology, and I have obtained. These have to do with reconstituted collagen. By reconstituted collagen I mean that the collagen is precipitated from a very fine dispersion of collagen fibrils which have been passed through a fine filter paper or other filtration medium. From such filtrates it is possible by various means to obtain collagen fibrils which present all of the fine structural characteristics which are to be seen in the native skin and other types of connective tissue.

About two years or more ago, a group of Russian workers began the study of buffer extracts of mammalian skin. They showed that it was possible to obtain a material from filtrates of such extracts, which they called procollagen, because they assumed this material to represent a biological precursor of collagen in the skin.

If, for example, a filtrate of a pH 4 citrate buffer extract of skin is dialyzed a precipitate is formed. On examining such precipitates in the electron microscope we found them to consist of material such as is shown in this slide. (Slide). You will observe the presence of normal collagen fibrils, and in addition, fibrils of a new type which show a much larger axial periodicity than ordinary collagen. We have called these "long spacing fibrils".

For a long time we have been puzzled by what this new type of fibrous structure might represent. I would like to show in the second slide (Slide) another example which was obtained from rat skin, and which shows the detailed fine structure found in these forms. A statistical study of the length of the period in the long spacing fibrils shows it to have a rather broad distribution, but with a well marked peak at about 2000 Angstroms.

We have found that we can produce these new types of fibrous structures at will by the addition of mucoprotein, obtained from bovine or human serum, to a soluble collagen filtrate, and dialysis of the mixture.

If, for example, a filtrate of a dilute acetic acid extract of ichthyocol, obtained from the collagenous tunics of the swim bladders of certain fish, is dialyzed against water, a loose gel is obtained which has the appearance in the electron microscope shown in the next slide. (Slide). As you see, it consistes merely of very fine amorphous filaments which show no discernible structure. If, however, a small percentage of mucoprotein has been added to such a filtrate, dialysis produces masses of large, well-formed long-spacing fibrils, as shown in the next slide. (Slide). With smaller proportions of mucoprotein, a mixture of long-spacing and normal fibrils is obtained, and with still smaller amounts the precipitate consists predominantly of normal fibrils.

It is our belief at the present time that the long-spacing fibrils represent a modification of collagen which does not exist in the native tissue—so far it has never been seen there—but which is formed under rather abnormal conditions. The role of mucoprotein in its production, however, and the possible involvement of mucoprotein in the formation of normal collagen fibrils under these conditions of reconstitution, raise large questions as to the nature of the normal collagen structure. We hope that further work of this kind will throw additional light on this subject.

A. N. KAY: In the slide which Dr. Borasky showed, the normal collagen showed the characteristic "fingerprint" of collagen. However, in the special technique, the CO_2 and pretanned fibers did not show the characteristic "fingerprint". Does that imply that you would change the surface by these tannages or by liquid CO_2?

R. BORASKY: The fibrils dried by the liquid CO_2 method have the characterisitic striations but could not be seen on the particular slide shown.

KAY: You do not suppose that fine structure is, in a sense, a symptom of stress caused during the drying?

BORASKY: The serrated edges characteristic of shadowed collagen fibrils may be due to a preferential loss of water from parts of the fibrils where the protein concentration is low and the water concentration is high. I believe Dr. Schmitt expressed the same idea several years ago. I do not believe that the fine structure, that is the period and intra-period bands are a symptom of stress caused during drying. X-ray diffraction data obtained from studies of moist collagen fibers show the same periodicity as shown by electron microscopic observations.

HIGHBERGER: It is possible to make wet replicas of fully hydrated fibrils and then examine the replica in the electron microscope. By this means Dr. Schmitt showed that collagen fibrils are essentially smooth cylinders, acquiring the serrated edges only on drying.

Influence of Splitting on the Strength of Chrome-Tanned Steer Sides*

By J. R. KANAGY, W. H. LESER, E. B. RANDALL, T. J. CARTER, and C. W. MANN†

National Bureau of Standards, Washington, D. C.

ABSTRACT

The effect of splitting on the strength of chrome-tanned steer sides having different average thicknesses was determined. The specimens for test were

*Presented at the Forty Seventh Annual Meeting, Groton, Conn., June 12, 1951.
This report is made as a part of the Leather Research Program sponsored by the Research and Development Branch, Military Planning Division of the Office of the Quartermaster General, Department of the Army. This program is under the Advisory Direction of the National Research Council.

†Present address, Leather Section, Office of the Quartermaster General, Washington, D. C.

selected by a statistical plan devised with the purpose of studying the effect of final thickness, the effect of original thickness or weight, and the effect of degree of splitting. Although the plan was directed toward the study of splits containing the grain, results were also obtained on the corresponding splits containing only the flesh layer.

The results indicate that the strength of the splits may be expressed as a function of either the final thickness or the degree of splitting. Original thickness within the range studied (131 to 93 mils) had no influence. The weakness of the grain layer is demonstrated by an extrapolation of the curve showing the variation of strength with thickness of grain splits. This curve intersects the zero strength line at a thickness value of 20 to 30 mils, which shows that the grain layer is much lower in strength than the other part of the hide.

The original leather as well as all of the splits show greater strengths when pulled in the direction parallel to the backbone than when pulled in the direction perpendicular to the backbone. The elongations at break are, however, greater for the perpendicular direction than in the parallel direction.

By the application of the least squares method, equations were obtained giving the relation of strength with thickness of split for each location (7 x 7 inch block) over the area of a side. With the use of this equation it will be possible to estimate the breaking strength and stitch tear of a split from its thickness, or select the thickness of split to give a definite strength value.

Introduction

Since the hides of cattle are composed of two different types of fibrous material having different physical properties, that of the grain and that of the reticular layer, it might be expected that the tensile strength is not uniform throughout the entire thickness. The outermost or grain layer, which contains the hair follicles and the thermostat mechanism in the living skin, is relatively weak, nearly all of the strength of the leather being in the reticular layer. Any reduction of the thickness of the leather by splitting would therefore tend to alter the tensile strength of the leather, and may either increase or decrease it per unit cross section, depending upon the part removed. It is, therefore, apparent that the extent to which leather is split in the process of manufacture will affect the strength.

The grain split of side leather from cattlehides is used in the manufacture of Army shoes, and therefore the degree to which the hides are split is influential in governing their quality and durability. Bowker and Olson [1] determined the strengths of the flesh and grain splits of vegetable-tanned steerhide sole and of chrome-tanned calf leathers. Since only one split was made, their results did not cover a wide range of thickness relations between grain and flesh splits. Wilson and Kern [2] have shown the relation between the strengths of the grain and flesh splits of vegetable- and chrome-tanned calf skins, but did not study heavy hides.

As a part of a large scale research program on the physical properties and sampling of upper leather in which 30 sides, split to the thickness required for Army shoe upper leather, are compared with 30 hides unsplit, it was decided to include a separate study on the effect of the degree or thickness of split on strength. Tensile strength and stitch tear were used as the criteria, since they are the tests on which the most information is available. Tests were made on splits of chrome-tanned leather containing the grain on which the thickness was varied systematically, and on the residual splits containing only the reticular layer.

Preparation of Specimens

Ten commercial chrome-tanned steer sides were used in this study. Sides having different thicknesses were selected so that information might be obtained on the influence of original thickness on the strength of the splits. The estimated weights (thicknesses), the determined average thickness in mils, and the area of the sides are given in Table 1. The chemical analysis of the leather is shown in Table 2.

TABLE I

Weight (thickness) and Areas of Hides Used in the Study of Splitting

No.	Area ft.²	Estimated thickness by wt. oz.	Estimated thickness equivalent mils	Actual thickness (avg.) mils
A	19	11	172	131
B	16	11	172	129
C	21¼	10	156	116
D	15½	10	156	121
E	16¼	9	141	120
F	21¼	9	141	119
G	15	8	125	107
H	16¾	8	125	113
J	14¾	7	109	93
K	14	7	109	95

In the sampling of the sides, the cutting area was determined as follows: A line parallel with the backbone was drawn so as to maintain a minimum distance of 21 inches between the backbone line and a parallel line in the shoulder area, and also to maintain, if possible, a minimum distance of 1 inch from the backbone line to the backbone edge. A line perpendicular to the backbone line was then drawn 2 inches from the root of the tail, and a line perpendicular to the backbone line was drawn at the shoulder approximately 4 inches from the neck, and subject to the condition that there was a minimum distance of 21 inches between the backbone line and a parallel line in the shoulder area as mentioned above.

TABLE 2

Composition of the Chrome-Tanned Upper Leather Used in the Study of the Effect of Splitting on Strength

(Results on dry basis)

Material	
Moisture %	13.9
Grease %	24.9
Hide Substance %	64.5
Ash %	4.3
Chromic Oxide (Cr_2O_3) %	4.1
pH	3.1

Seven by seven inch blocks were then cut from the cutting area. The number of these blocks cut depended, of course, upon the size of the sides. The backbone line between the parallels was measured, and if the distance was 63 to 69 inches, nine blocks were cut in the first row. If the distance was 69½ inches or more, 10 blocks were cut. The same procedure was used in determining the number of parallel rows of blocks. If the distance from the backbone line to the belly was 21 inches, only 3 rows of blocks could be cut. However, in several sides the distance was 28 inches or more at the butt and the belly. This permitted several more blocks in these sides. A diagram of a side cut into blocks is shown in Figure 5.

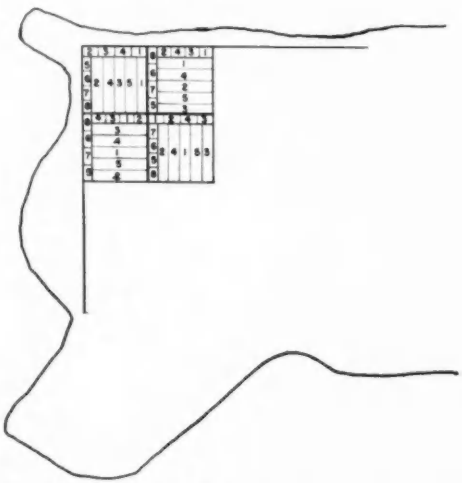


FIGURE 1—Plan used to cut tensile and stitch tear specimens from 7 x 7 inch blocks.

Tensile and stitch tearing strength determinations were made in directions parallel and perpendicular to the backbone. The method used in sampling is given in the diagram shown in Figure 1. For the purpose of determining in which blocks the tensile specimens should be perpendicular or parallel, the sides were separated at random into two groups of five. The five sides in group 1 had tensile specimens cut perpendicular to the backbone line in the initial block (backbone butt corner). The five sides in group 2 had tensile specimens cut parallel to the backbone line in the initial block. The direction of test specimens in the other blocks was alternated, both row wise and column wise, starting from the initial block.

Five tensile specimens were cut from the 6 x 6 inch block left after the stitch tear strips were taken from the backbone and butt sides. These consisted of three grain splits interspaced with two unsplit controls. The unsplit controls, as shown in the figure, were numbered 4 and 5 and were always taken from the same relative positions in the block. The grain split specimens were numbered 1, 2, and 3, of which 1 was the thickest, 2 the next thickest, and 3 the thinnest. The positions of the split specimens were chosen by means of random numbers. As shown in Figure 1, the stitch tear specimens were cut from 6- or 7-inch strips taken from the sides of the blocks nearest the backbone and butt. The stitch tear was determined by pulling in a direction parallel with the longer side of the specimen, and therefore it was possible to make this determination in both directions on each block.

The 7-inch strip from each block was cut into four stitch tear specimens, 1.75 inches long; the 6-inch strip from each block was cut into four specimens, 1.5 inches long. The four specimens taken from the backbone edge of the block were assigned the numbers 1–4 in random order; the four from the butt edge of the block were assigned the numbers 5–8 in random order. Specimen numbers 1 and 5 are the thickest grain splits, 2 and 6 the next thickest, 3 and 7 the thinnest grain splits, and specimens 4 and 8 the controls for their respective strips.

All blocks, regardless of the hide from which they originated, were divided into six groups according to initial thickness, as shown in Table 3. These six groups of blocks were then cut up into strips for tensile strength and stitch tear tests according to the random selections mentioned previously.

The specimens were split to different thicknesses depending upon the minimum thickness of the blocks, unless otherwise stated, by means of a belt-knife splitter. All split specimens to which reference is made contain the grain layer. The different thicknesses to which the specimens were split were selected to coincide as nearly as possible with the range of the upper leather now being used for Army shoes. The upper limit was therefore approximately 96 mils and the lower limit 40 mils. All split specimens, regardless of the thickness of the unsplit specimens from which they originated, were divided into eight groups, the difference in thickness between successive groups

TABLE 3

Plan Used in Distributing Unsplit Blocks into Split Groups.

Grouping of unsplit specimens					Grouping of split specimens	
Thickness mils	Unsplit group No.	No. of blocks in group	Tensile specimen*	Stitch tear specimen*	Thickness mils	Split group No.
130+	I	68	1	1 and 5	96	1
			2	2 and 6	80	3
			3	3 and 7	64	5
110 to 129	II	51	1	1 and 5	88	2
			2	2 and 6	80	3
			3	3 and 7	72	4
95 to 109	III	31	1	1 and 5	80	3
			2	2 and 6	64	5
			3	3 and 7	48	7
86 to 94	IV	43	1	1 and 5	72	4
			2	2 and 6	64	5
			3	3 and 7	56	6
72 to 85	V	51	1	1 and 5	64	5
			2	2 and 6	56	6
			3	3 and 7	48	7
71–	VI	37	1	1 and 5	56	6
			2	2 and 6	48	7
			3	3 and 7	40	8

*Tensile specimens 4 and 5 and stitch tear specimens 4 and 8 were the unsplit controls.

being about 8 mils. As the specimens containing the grain were split from the flesh, they were marked for identification. The specimens containing only the flesh were marked on the side nearest the grain with the number of the piece from which they were cut.

After the tensile specimens were split, they were cut into dumb-bell shape for testing. Tensile strength and stretch were determined according to Method 240.1 in Federal Specification KK-L-311, and stitch tear was determined by Method 246.2 in the same specification.

Results and Discussion*

In the following sections of this paper, average results of the tests on all of the hides are first presented. These are then broken down to give the results obtained from tests in the two different directions, then average results are given for several locations representing differences in the fiber structure, and finally results are given for the individual blocks.

An attempt is made to present some of the results in such a way that the tanner would be able to determine what thickness was necessary to give a certain desired strength value. The limits of significance were determined

*A thorough statistical study of the tensile strength data given in this paper will be presented in the National Bureau of Standards Journal of Research.

where it was essential, and some fundamental and theoretical relations are discussed.

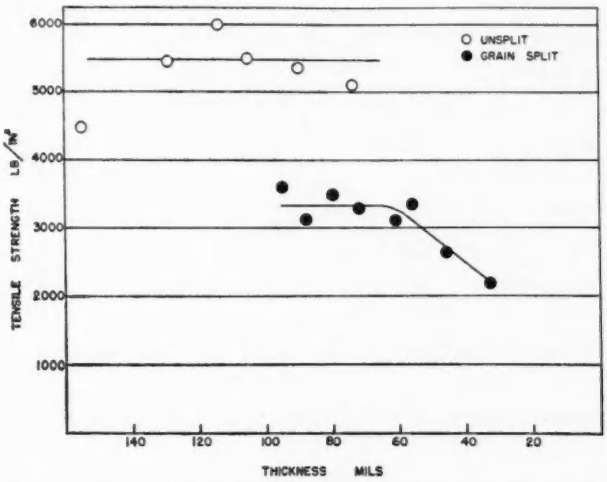


FIGURE 2—Comparison of the tensile strengths of the split and unsplit control specimens (Results are averages of tests in both parallel and perpendicular directions)

The results for the tensile strengths of the split leather containing the grain and the unsplit control samples are given in Figure 2. These results are averages obtained from the tests in both parallel and perpendicular directions.

Average values for the six groups of unsplit leather grouped according to thickness, and average values for the eight groups of split leather are given. The tensile strength of the unsplit leather is not constant and does not follow a straight line as might be expected. Specimens having thicknesses of about 115 mils appear to be stronger than the others. This is undoubtedly the influence of location. Locations tend to be grouped when thicknesses are grouped, and no definite effort was made in these tests to eliminate this effect of location for the unsplit leather. Split samples show lower tensile strengths than the unsplit specimens even when they have the same thickness. The split samples show uniform strengths when calculated on a thickness basis above a minimum thickness of 60 mils. Below 60 mils tensile strength decreases rapidly with decrease in thickness.

Breaking strength values for the split leather containing the grain and the unsplit specimens are given in Figure 3. These are also average values for both parallel and perpendicular directions. The circles give average values for each of the six unsplit and the eight split groups. The broken lines drawn

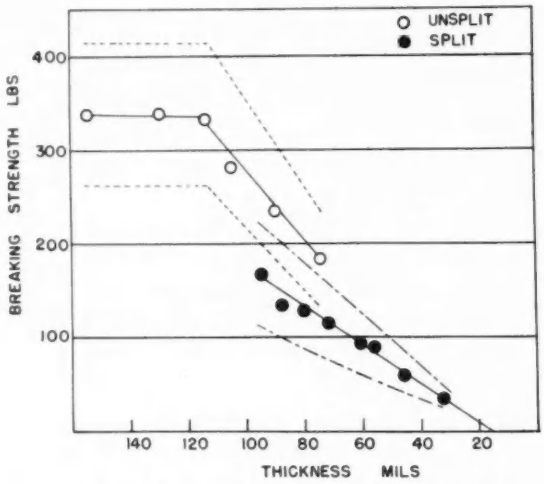


FIGURE 3—Comparison of the breaking strengths of the split and unsplit control specimens. (Results are averages of tests in both parallel and perpendicular directions.)

above and below the curve for the average values give an indication of the variability of the results. They show the boundary line of one standard deviation below the average and one standard deviation above the average. This means that approximately 68 per cent of the values corresponding to each point may be expected to lie between the two broken lines. Sixteen per cent are above the top broken line and 16 per cent below the bottom broken line. This graph may be used to determine the thickness to which leather should be split in order to obtain a certain breaking strength. For a thickness of about 90 mils, 84 per cent of the specimens will have a breaking strength of 100 pounds or more. For a thickness of 60 mils, the average is about 90 pounds and 16 per cent of the specimens are below 60 pounds. The breaking strength appears to decrease in a straight line as a function of thickness for the unsplit samples below 115 mils; above this thickness the average breaking strength is constant. The breaking strengths for the split samples decrease according to a straight line function of thickness and strength, and if the curve is extrapolated it intersects the line for zero strength at about 20 mils. This shows the influence of the grain layer on the strength properties of the leather.

Values for the breaking strengths of unsplit and split leathers tested parallel and perpendicular to the backbone are given in Figure 4. The strengths determined in the parallel direction are higher in all cases. The unsplit specimens show the greatest differences. These differences are greatest at thickness-

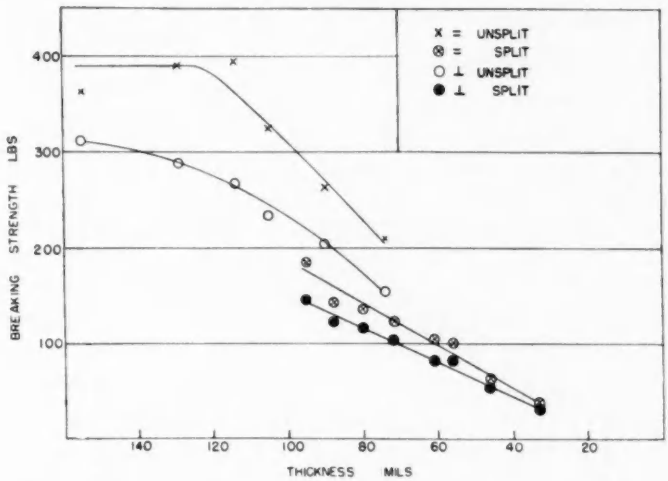


FIGURE 4—Comparison of the breaking strengths of the split and the unsplit control specimens in the parallel and perpendicular directions of test.

es ranging from about 110 to 130 mils, which is pointed out in the discussion of Figure 2 as undoubtedly a function of location. Strength values for unsplit leather obtained in the perpendicular direction fall on a smooth curve which decreases gradually with thickness. This indicates that strength values determined in the perpendicular direction may be more uniform and less variable than those determined in the parallel direction. The breaking strength of the splits cut in either direction appear to be approximately a straight line function of thickness, and on extrapolation the curves intercept the 0 strength line at approximately the same point (20 mils).

In Figure 5 are given the tensile strengths in the two directions for the various locations over the area of a side for the controls 0 and the 1, 2, and 3 splits. The thicknesses of the specimens are also given. These are average values for all of the 10 sides. Except for the butt areas, the strength in the parallel direction appears to be considerably greater than that in the perpendicular direction. The greatest difference in the two directions of test appears to be the belly areas about half way between butt and shoulder.

Breaking strengths as a function of thickness for various locations over the area of the side are given in Figures 6 and 7. The locations presented were selected to represent as nearly as possible all of the widely different types of fiber structure found over the area of the side. Figure 6 shows the breaking strength in the perpendicular direction, whereas Figure 7 shows it in the parallel direction. These curves, if extrapolated, would intersect the 0 strength line

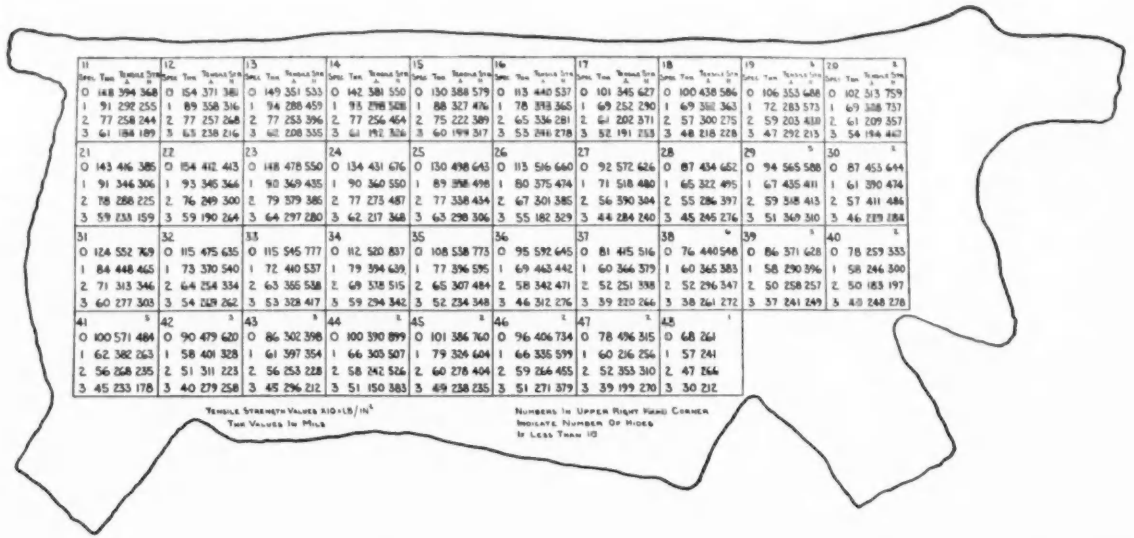


FIGURE 5—Tensile strengths in the two directions of test for the various locations over the area of a side for the controls 0 and the 1, 2, and 3 splits. (Results are averages of all the sides tested.)

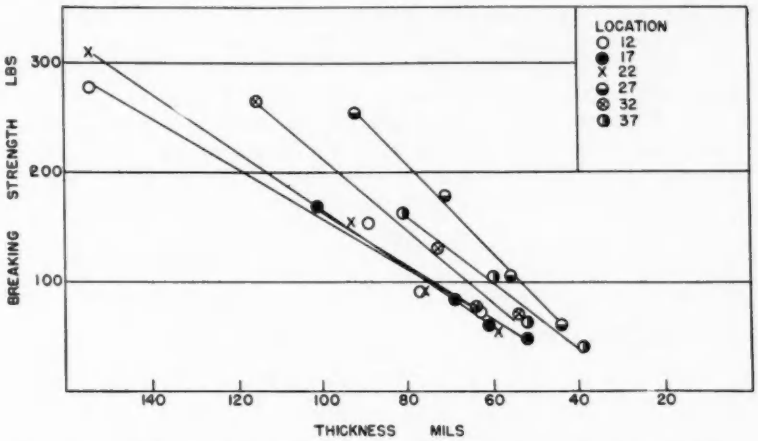


FIGURE 6—Breaking strengths in perpendicular direction of test for various locations over the area of a side.

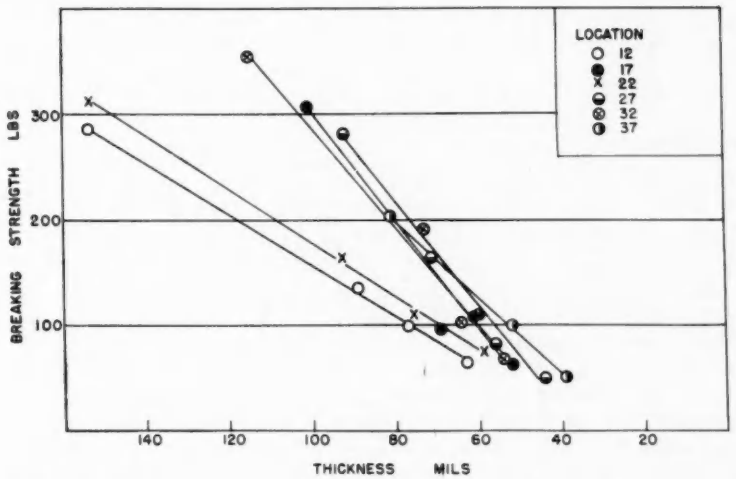


FIGURE 7—Breaking strengths in parallel direction of test for various locations over the area of a side.

at about 30 mils thickness on the average, rather than 20 mils as was shown in Figures 3 and 4 where average results for the split specimens in all locations were shown. The reason for the difference probably lies in the method used

for grouping the specimens. The intercepts obtained from the results of the block averages are most reliable, since the variation due to location is eliminated and each point is composed of the average results of a definite proportioned split, namely, either the 1, 2, or 3 split or the unsplit.

The differences between the results for the perpendicular and for the parallel directions lie mainly in the fact that the belly and shoulder locations show much greater strength in the parallel direction. For the same thickness, shoulder and belly locations give stronger leather than butt locations.

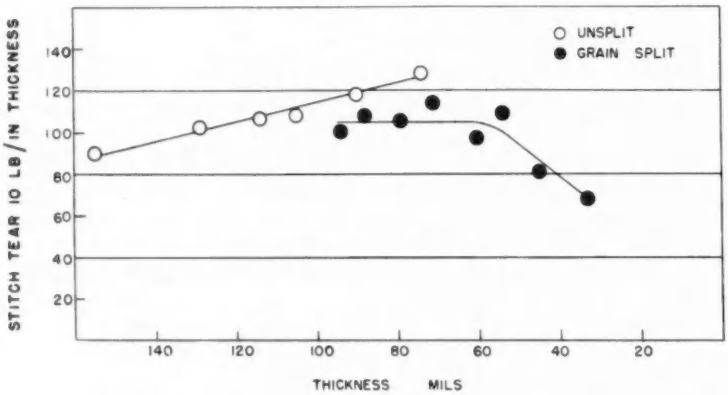


FIGURE 8—Comparison of the results of the stitch tear tests, based on pounds per inch of thickness, of the split and unsplit control specimens. (Results given are averages of both parallel and perpendicular directions of test.)

Results of the stitch tear tests based on pounds per inch of thickness are shown in Figure 8. In these tests the unsplit samples show an increase in strength with decrease in thickness, which may in part be caused by the effect of location but mostly by the mechanism of the test. The split samples show uniform strength based on a unit of thickness down to about 55 mils, at which point an abrupt decrease in strength occurs. If the stitch tear in pounds is plotted against thickness, both the unsplit and split samples fall approximately on the same curve (Figure 9). This curve is parabolic in shape indicating that stitch tear tends to approach a maximum value and the 0 strength line is intercepted at about 20 mils thickness. A close examination of the curve shows that for the split specimens down to 50 mils thickness the average strength approximates one pound per mil of thickness.

The broken lines in Figure 9 show the limits for one standard deviation above and below the average, as shown for the breaking strength in Figure 4. Approximately 68 per cent of the specimens will have strengths lying between

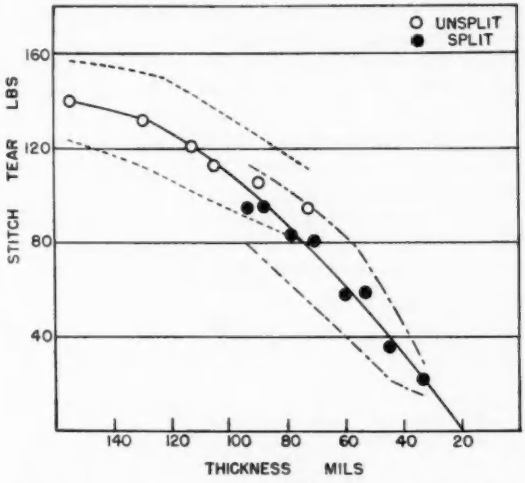


FIGURE 9—Comparison of the results of the stitch tear in pounds for split and unsplit control specimens. (Results given are averages of both parallel and perpendicular directions of test.)

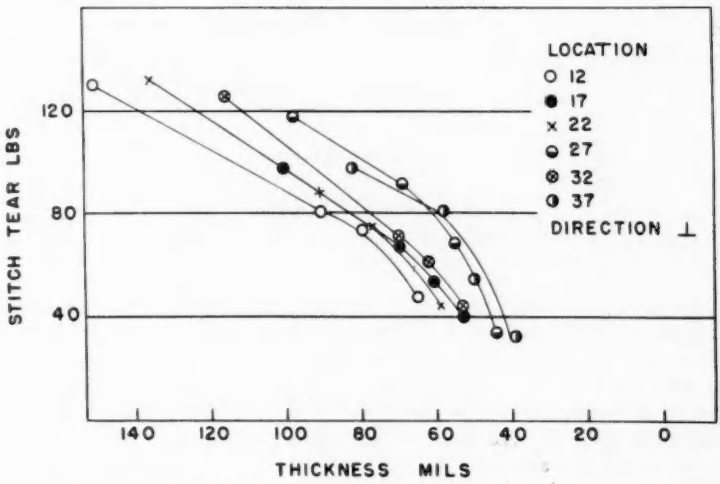


FIGURE 10—Results of stitch tear in pounds for various locations over the area of a side. Tests made in perpendicular direction.

the two broken lines, and all other aspects of the statistical analysis are similar to those described previously under Figure 4.

The variations of stitch tear in pounds for various locations with thickness are given in Figures 10 and 11. Figure 10 gives the values determined in the perpendicular direction and Figure 11 gives those determined in the parallel direction. In contrast to the results of the breaking tests there appears to be little difference on the average between the two directions of test for stitch tear. Both figures show a curvilinear relationship between stitch tear strength and thickness. All of the curves are similar in slope to the one shown for the average of all the tests in Figure 9. The intercept at the 0 strength point appears to be at about 30 mils, which is approximately the same point as that for the breaking strength values.

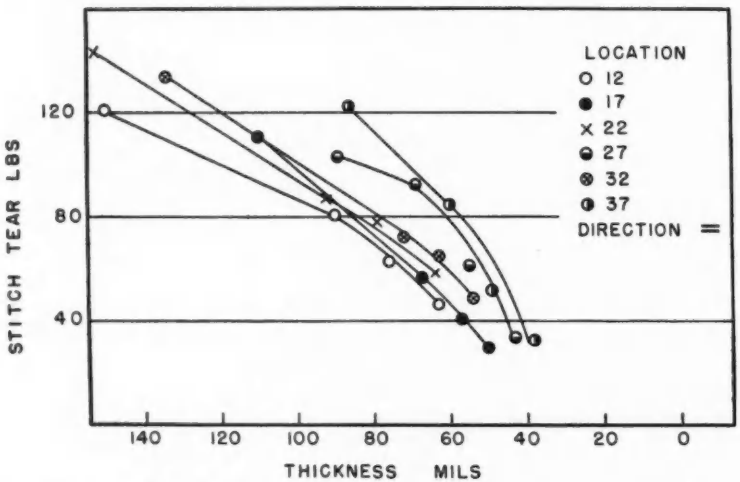


FIGURE 11—Results of stitch tear in pounds for various locations over the area of a side. Tests made in parallel direction.

The stitch tear values per inch of thickness over the entire area of a side are given in Figure 12. These results are fairly uniform over the entire area. On the average for a side the stitch tear values are the same in the perpendicular direction as in the parallel direction. In some locations a very definite directional difference is noted, however. The split samples when put on a unit thickness basis have about the same strength, above 55 mils thickness, as the unsplit specimens.

The tensile break and stitch tear strengths for the flesh splits are compared with those for the grain splits in Figures 13 and 14, respectively. The flesh

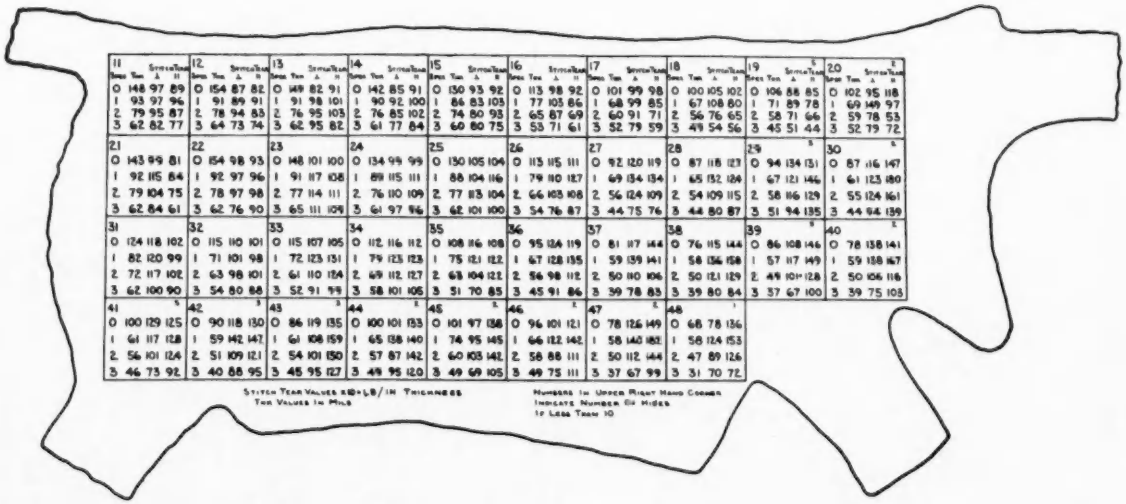

11 12 13 14 15 16 17 18 19 20
21 22 23 24 25 26 27 28 29 30
31 32 33 34 35 36 37 38 39 40
41 42 43 44 45 46 47 48
Stitch Tear Values #lb/in Thickness
Top Values In Mils
Numbers In Upper Right Hand Corner
Indicate Number Of Mils
If Less Than 10

FIGURE 12—Stitch tear values per inch of thickness in the two directions of test for all locations over the entire area of a side. Results are averages for all sides.

splits in all cases are stronger than the grain splits. The breaking strength averages about 40 pounds higher, whereas the stitch tear averages about

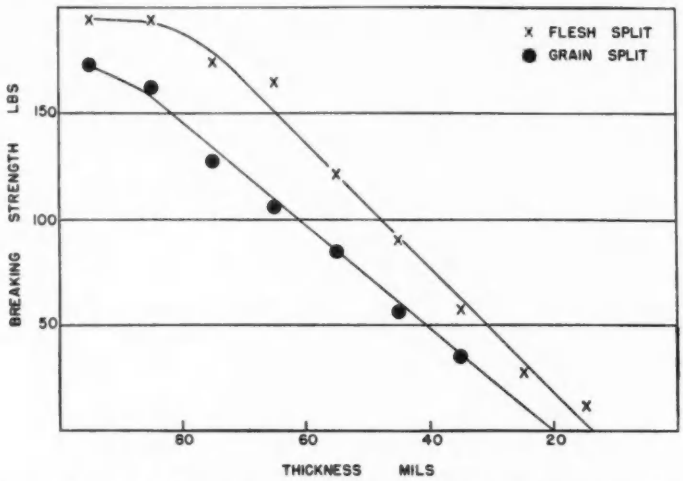


FIGURE 13—Comparison of the breaking strengths of the flesh and grain splits. (Results are averages of tests made in both directions.)

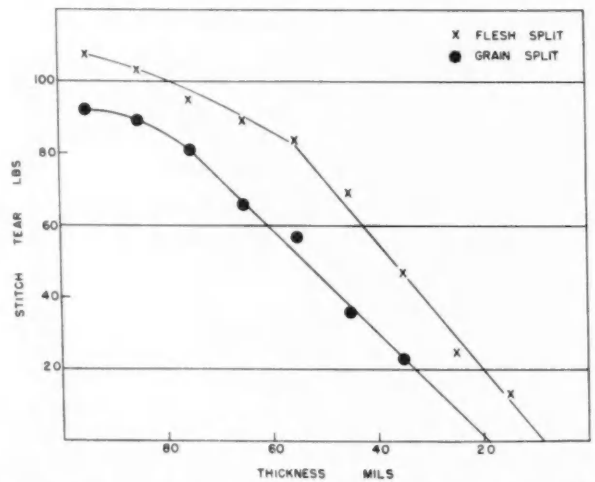


FIGURE 14—Comparison of the stitch tear strengths of the flesh and grain splits. (Results are averages of tests made in both directions.)

30 pounds higher. On extrapolation, the curve showing the results for breaking strength intercepts the 0 strength curve at about 15 mils, whereas the one showing the results for the stitch tear strength intercepts at about 10 mils.

Intercepts were calculated by means of least squares from a plot of strength in pounds against thickness for breaking and stitch tear. The average values for the 10 hides for the original leather and the 1, 2, and 3 splits were used. The intercepts were determined for each block in the hide so that it might be possible to determine the exact thickness of split to give a definite desired strength at any location. These results are given in Table 4 in terms of slope (m), y intercept (b), and the x intercept.

The results may be applied by substituting the pertinent values in the equation: $y = mx + b$, where y is the strength in pounds, m is the slope, x is the thickness, and b is the y intercept. The equation may be used to obtain an estimate of the strength if the thickness is known, or for estimating the necessary thickness required for a definite strength. The x intercepts are of importance because they are related to the grain thickness or that part of the grain surface having extremely low strength.

The x intercepts for the breaking strengths are quite uniform. Averages for each of the three rows of blocks in both directions of test are in the range 30 to 35. Considerably more variation is, however, in evidence for the stitch tear results, and the x intercepts appear to be much lower. This is because, as shown in Figures 10 and 11, the curve showing the relation of stitch tear and thickness is curvilinear. The assumption of a straight line in the least squares method, therefore, gives inaccurate values for the intercepts. It can, however, be observed that the intercepts on the 0 strength line in both figures will be in the range of 30 to 40 mils. The data given in Table 4 may be used to estimate the stitch tear strength for a certain thickness of leather. This estimation will not be quite as reliable as it is for the breaking strength. The reliability will, however, increase with increasing thickness of split.

General Discussion

The results of the tests show that the strength of leather on splitting, allowing for location variations, varies in linear fashion with thickness. Figure 6 shows that locations from the belly are stronger per unit thickness than the butt locations. However, upon splitting the strength for both appears to decrease equally in proportion to the percentage of the original thickness removed. The curves indicating breaking strength approach each other as the thickness decreases. The belly locations remain slightly stronger when split thin. On extrapolation to 0 strength, the curves for all locations would intersect at approximately the same point. This is an indication that the grain may have approximately the same thickness over the entire hide.

A correlation between final thickness and tensile breaking load and degree of splitting (percentage of original thickness removed) and tensile breaking

TABLE 4

Calculated Constants Showing Relation between Thickness of Split and Strength

	Breaking Strength						Stitch Tear					
	Perpendicular			Parallel			Perpendicular			Parallel		
Location	m	b	x intercept	m	b	x intercept	m	b	x intercept	m	b	x intercept
11	2.49	- 94.1	37.8	2.34	- 90.6	38.7	1.05	- 9.8	9.4	0.97	- 7.9	8.1
12	2.24	- 72.5	32.4	2.28	- 71.1	31.2	0.88	- 1.9	2.2	0.82	0.5	-0.61
13	2.12	- 68.6	32.4	3.16	- 91.8	29.1	0.75	11.1	-14.8	0.90	4.7	- 5.2
14	2.33	- 80.9	34.7	3.29	- 90.1	27.3	0.88	- 2.3	2.6	0.88	5.7	- 6.4
15	2.46	- 85.5	34.8	3.95	-151.8	38.4	1.02	-14.4	14.1	1.00	- 5.9	5.9
16	2.79	- 82.9	29.7	3.44	-119.2	34.6	1.17	-19.8	16.9	1.11	-22.4	20.3
17	2.45	- 90.3	36.9	4.12	-137.4	33.3	1.13	-14.8	13.0	1.22	-28.4	23.3
18	2.91	- 84.7	29.1	4.19	-159.5	38.1	1.62	-48.7	30.0	1.38	-40.5	29.3
Ave.	2.47	- 82.4	33.5	3.35	-113.9	33.8	1.06	-12.6	9.2	1.04	-11.8	9.3
21	2.60	- 92.2	35.5	2.48	- 93.1	37.5	1.07	- 3.9	3.6	0.91	-12.8	14.1
22	2.62	- 95.7	36.5	2.33	- 59.7	25.6	1.09	-13.9	12.8	0.88	5.5	- 6.3
23	2.95	- 98.7	33.4	3.29	-109.0	33.1	0.87	20.2	-23.2	0.90	15.0	-16.6
24	2.80	-102.7	36.7	4.21	-141.9	33.7	0.91	12.7	-13.9	0.93	9.4	-10.1
25	3.32	-122.4	36.9	4.40	-171.0	38.9	1.02	3.0	- 2.9	1.02	4.0	- 3.9
26	3.58	-143.0	40.0	4.78	-183.8	38.4	1.39	- 2.3	1.6	1.23	- 9.8	7.9
27	4.02	-117.3	29.2	4.42	-144.2	32.6	1.46	-18.8	12.9	1.51	-24.1	16.0
28	3.12	- 93.6	30.0	4.57	-137.2	30.0	1.55	-25.5	16.4	1.52	-19.8	13.0
Ave.	3.12	-108.2	34.8	3.81	-130.0	33.7	1.17	- 3.6	0.9	1.11	- 4.1	1.8
31	3.89	-152.5	39.2	4.57	-191.0	41.8	1.31	-11.4	8.7	1.03	- 2.9	2.8
32	2.75	- 75.4	27.4	3.91	-132.7	33.9	1.26	-19.1	15.1	1.02	- 2.4	2.3
33	3.10	- 84.0	27.1	4.34	-113.5	26.2	1.15	- 4.0	3.5	0.94	16.1	-17.1
34	3.57	-123.7	34.7	5.78	-220.2	38.1	1.24	- 6.0	4.8	1.03	11.9	-11.5
35	3.59	-122.1	34.0	5.13	-167.7	32.7	1.49	-30.1	20.2	1.08	2.2	- 2.0
36	3.43	- 84.8	24.7	4.20	-120.6	28.7	1.49	-21.4	14.3	1.29	- 8.6	6.7
37	2.69	- 66.8	24.8	3.48	- 82.5	23.7	1.49	-18.6	12.5	1.90	-37.4	19.7
38	3.64	-106.5	29.3	3.68	- 93.7	25.5	1.68	-29.5	17.6	1.70	-19.6	11.5
Ave.	3.33	-102.0	30.2	4.39	-140.2	31.3	1.39	-17.5	12.1	1.25	- 5.1	1.6
Hide Ave.	2.97	- 97.5	32.8	3.85	-128.0	32.9	1.21	-11.2	7.4	1.13	- 7.0	4.2

load was made. The value for the former was 0.86, whereas that for the latter was 0.83. This indicates that either one of the two criteria give a good correlation with breaking load, and shows further the importance of the final thickness on the strength.

Weight of side within the range used in this work, 131 mils to 93 mils, has no influence on the tensile strengths of the split leathers. The thicknesses of the sides in mils are given in Table I. The sides were lettered starting with A for the heaviest side and ending with K for the lightest. In Figure 15 are shown the tensile strength values for all of these sides, for split thicknesses from 30 to 100 mils. Values for each side in a range of 10 mils thickness were averaged, for example 90–99, 80–89, etc. If thickness of the original side had any influence on strength, then the curves showing the variation of strength with side should show either a rise or a drop in going from side A to K. It may be noted from the figure there is no trend in either direction. There appears to be an average overall straight horizontal line relation from A to K. The results do, however, show a decrease in strength with decrease in thickness. This decrease, on the average, appears to be uniform for all of the sides regardless of original weight.

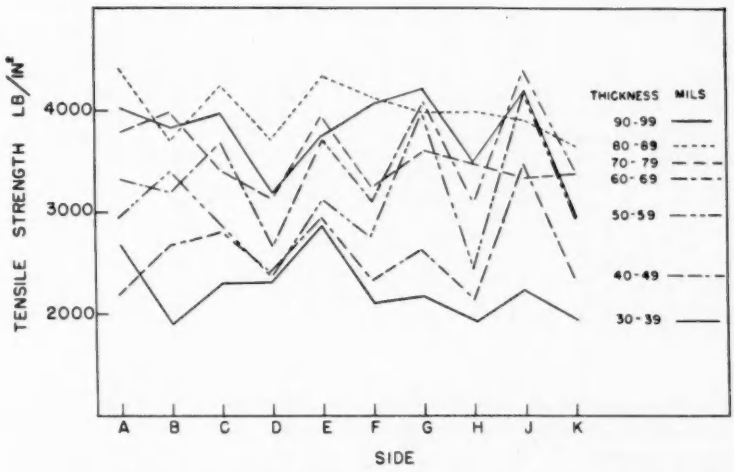


FIGURE 15—Variation of tensile strengths from heaviest to lightest weight side for unsplit controls and splits.

The average tensile strength in the parallel direction is greater than that in the perpendicular direction for each side for both unsplit and split leathers. The percentages of stretch are, however, greater in the perpendicular direction

TABLE 5

Tensile Strength and Stretch of Grain Splits and Unsplit Chrome-Tanned Steer Hides

	Unsplit				First split (heavy split)				Second split (medium split)				Third split (light split)			
	Strength lb/in²		Stetch %		Strength lb/in²		Stretch %		Strength lb/in²		Stretch %		Strengt lb/in²		Stretch %	
Hide	⊥	//	⊥	//	⊥	//	⊥	//	⊥	//	⊥	//	⊥	//	⊥	//
A	443x10	575x10	69	51	364x10	474x10	81	58	313x10	418x10	84	61	277x10	273x10	78	56
B	442	590	63	50	357	465	70	53	307	379	65	56	270	314	73	53
C	459	642	68	48	344	440	69	50	282	380	69	55	254	303	66	49
D	406	541	74	57	318	391	85	66	254	279	82	64	210	223	70	52
E	495	612	66	52	386	455	71	57	342	415	67	51	297	332	65	46
F	444	545	64	48	348	424	72	54	299	344	69	57	212	298	67	52
G	441	578	68	54	392	480	69	65	308	434	76	59	262	303	78	62
H	444	567	68	55	352	412	77	58	235	360	75	56	222	252	68	53
J	500	673	65	53	447	457	70	58	340	394	72	56	225	263	65	51
K	429	595	71	49	331	457	71	51	233	337	73	47	214	255	70	47
Ave.	450	592	68	52	364	446	74	57	291	374	73	56	244	282	70	52

than in the parallel direction. These values for each side for the unsplit and split leathers are given in Table 5. The first split shows a significant increase in stretch over the unsplit in both directions. The difference between the stretch values for the first and second splits is not significant. The third split shows a significant decrease from the second split in stretch for the parallel direction, and the decrease in the perpendicular direction is possibly significant. The increase in stretch for the first and second splits is caused by greater ease of slippage, since many fiber ends have been cut. In the third split stretch is lower because the loads at break are also much lower.

Values for each side for stitch tear in parallel and perpendicular directions are given in Table 6. No appreciable difference in strength with direction of test is shown in the average values. The first and heaviest split is slightly higher in stitch tear on a unit thickness basis than the original leather, the second split is about equal in strength, and the third or thinnest split is lower in strength.

TABLE 6

Stitch Tear Strength of Split and Unsplit Chrome-Tanned Steer Hides

	Unsplit		First Split (heavy split)		Second Split (medium split)		Third Split (light split)	
Hide	strength ⊥	lb./in thk. //	strength ⊥	lb./in thk. //	strength ⊥	lb/in thk. //	strength ⊥	lb/in thk. //
A	103x10	98x10	113x10	117x10	104x10	112x10	95x10	96x10
B	106	107	120	118	109	115	90	103
C	115	117	115	120	105	105	84	89
D	96	98	104	100	89	86	70	73
E	107	104	116	109	103	107	96	92
F	110	111	114	122	99	112	87	92
G	96	102	103	102	102	99	82	78
H	102	106	105	106	93	93	67	74
J	119	119	136	128	119	112	79	80
K	107	114	103	115	89	89	67	70
Average	106	108	113	114	101	103	82	85

The differences in the trends of the strength values for stitch tear and breaking load on splitting have been pointed out several times in this report. Tensile strength shows an abrupt decrease when the leather is split, whereas the change in stitch tear appears to be no greater than that which would be expected from a certain decrease in thickness.

The fundamental difference in the application of the two tests is that in the tensile strength test a load is applied over a much larger area than in the stitch tear test. The opportunity for obtaining full effect of orientation is therefore at a maximum in this test, and the influence of any cut fiber ends

will also be noticed. In the stitch tear test a stress is concentrated over a much smaller area and fewer fibers are involved. The chance for obtaining full effect of orientation is at a minimum and cut fiber ends may not be involved. Since only a few fibers are torn at any one instant in the stitch tear test, the full thickness of the leather may not be involved. Maximum strength may correspond with the load required for tearing the maximum number of fibers which may become involved at the instant of tear. This may not be a function of thickness. A mechanism of this type explains why the curve showing the increase in stitch tear strength with increase in thickness flattens out and appears to approach a maximum.

References

1. R. C. Bowker and E. S. Olson. *J. Am. Leather Chem. Assn.* **25,** 275 (1930).
2. "Modern Practice in Leather Manufacture" by John Arthur Wilson, pg. 651, Reinhold Publishing Corp., New York, N. Y. (1941).

Received Feb. 9, 1952.

Discussion

M. Maeser: Dr. Kanagy has brought out three points that are different than some of the notions that many of us have regarding leather.

First, I believe it has been generally felt that the breaking strength of leather would decrease very rapidly as the percentage of the leather which was split off increased.

If I understand Dr. Kanagy right his paper has demonstrated that when a thin flesh split of a half ounce or so of leather is taken from skin, there is an immediate loss in breaking strength, even though the amount of material removed has been small. But then, as the leather is split further the breaking strength decreases in a manner proportional with the remaining thickness of the piece.

Something seems to happen on the initial split that affects the strength considerably, but as splitting is continued, the breaking strength is directly proportional to the amount of leather which is left.

This raises a little contradiction to our common conceptions, and will not hold true over the whole range of leather thickness..

If you noticed in next to his last slide, Dr. Kanagy gave values which showed a rather marked decrease in tensile strength as the splitting continued.

If, as the grain becomes a larger proportion of the total sample, the tensile strength does decrease, then one would expect that the breaking strength might remain proportional to the thickness until some critical value of thickness had been reached, and as splitting continued from there on down, the breaking strength curves should take a dip downward. Dr. Kanagy, will you explain why, if your tensile strength actually does reduce as your thickness decreases, you did not get a curve rather than a straight line between thickness and breaking strength?

J. R. KANAGY: You will not get a curve until the splitting reaches the point where the grain becomes a much larger proportion of the total thickness of the specimen, a point that we did not consider it necessary to reach in this work. Then you would probably get a slight curve down to the origin on the graph. It is not strictly correct to assume that the grain has absolutely no strength. It does have a small amount of strength, though for most practical purposes it is negligible. That is why I drew the straight line. It is much easier to interpret the straight line as a practical matter, rather than to introduce the complications of a curve down to the origin for the thin grain splits.

I think the equation I presented can be used to advantage for calculating the average thickness. At least, it gives some basis to use in producing leather of the strength desired for any particular use.

MAESER: If you will notice the breaking strength curves between eight ounces and three and a half ounces to four ounces, there is no doubt that his statement is correct. That is the range of thicknesses of most of our leathers.

The second interesting thing is that the product of the tensile strength and the stretch of leather when cut either parallel or perpendicular to the backbone is a constant. That means, of course, that the energy of fracture is not affected by direction.

Without further study, I don't know that we can interpret that into any practical meaning, but it might have something to do with the phenomenal resistance which leather has to repeated stresses or deterioration due to fatigue. But at this time I do not think we can be sure.

The third point which he brings out, I wanted to emphasize, because I am a member of the Physical Testing Committee. We often think we have too many strength tests, that tensile strength is the only one we need.

Dr. Kanagy's work shows that stitch tear and tensile strength do not vary in the same manner over a series of leathers and they probably do not measure the same property of leather. It does not neccessarily follow that a leather which is strong in tension will also have high stitch tear values.

R. M. KOPPENHOEFER: I would merely say on stitch tear and tensile strength that there seems to be quite a difference in those two tests. They certainly do not measure the same thing, because the stitch tear responds very beautifully to lubrication, whereas the tensile does not vary over nearly as wide a range, and is more difficult to interpret.

E. B. THORSTENSEN: I would just like to add a word. I agree with Dr. Koppenhoefer that no relationship exists, because the simple test that most Army inspectors make is to cut a strip near the edge, and if it does not tear, it has good stitch tear resistance.

Sampling of Side Upper Leather II*†

By C. W. Mann**, John Mandel, Mary N. Steel, and J. R. Kanagy

National Bureau of Standards
Washington 25, D. C.

Abstract

A procedure for the sampling of side upper leather for physical and chemical tests has been developed. This procedure is based on the results obtained from tests on 90 sides of side upper leather. In these 90 sides were included all of the variables generally associated with this type of leather, such as type of tannage (straight chrome or vegetable retan), splitting (split or unsplit leather), and sex of the animal from which the side was taken (cow or steer).

The selection of the sampling location was based on the correlation between the value obtained for a specific test for a block and the average for that test in the corresponding side. For each test, it was found that several blocks gave high correlation coefficients and consequently would be suitable for this test. The most suitable location for sampling for all tests required in acceptance testing was also determined. A procedure for setting minimum values for strength in specifications is described.

Introduction

Recently a paper [1] was published in the Journal of the American Leather Chemists Association which gave the preliminary work on the sampling of side upper leather. As was stated in this paper, the purpose of the work was to determine the most desirable sampling procedure for about 100 different lots of leather in a study of the physical and chemical characteristics of chrome retanned upper leather. The work consisted in determining the physical and chemical properties of 30 sides of split chrome-tanned leather. Rankings of side positions for sampling for tests in tensile strength, stitch tear strength, tongue tearing strength, bursting strength, density, water vapor permeability, water penetration, chromic oxide, hide substance, and grease were given. The side to side variability for these tests was also given, together with average results for most of the tests for all positions.

In order to increase the reliability of the results, the work to which reference was made [1] has been extended to include studies with 30 sides of

*Presented at the Forty Seventh Annual Meeting, Groton, Conn., June 11, 1951.

**Present address: Office of the Quartermaster General, Washington, D. C.

†This report is made as a part of the Leather Research Program sponsored by the Research and Development Branch, Military Planning Division, Office of the Quartermaster General, Department of the Army. This program is under the Advisory Direction of the National Research Council.

unsplit upper leather, 15 chrome retanned steer sides, and 15 chrome retanned cow sides. The final results of this study, which are presented in this paper, are based on the leathers just mentioned and the 30 sides of split chrome tanned leather on which results were given in the previous paper.

Leathers

The work on sampling described in [1], was based on 30 sides of chrome tanned leather split to the thickness generally used for upper leather. This leather was chosen initially because it was thought that the variations in the physical properties of leather were inherent in the original hide structure and that the chrome tannage would alter these the least. The 30 unsplit sides for which results are given in this paper were the opposite sides from the hides from which the split leathers were obtained. This procedure was followed in order to determine as nearly as possible the effects of splitting alone. The unsplit leathers were also straight chrome tanned. The 15 cow and 15 steer sides which were split and retanned by the process ordinarily used for upper leather were chosen to find out if any differences might exist because of the sex of the animal, and also to determine if the sampling procedure applied to chrome tanned leather might also be applied to chrome retanned leather. The 90 sides used in this study therefore are a cross section of the different types of tannages and types of animals which would probably be included in leather of the side upper type.

Plan of Experiment

The method used to cut the sides into blocks and the method of cutting specimens from these blocks are described in [1] and shown in Figure 1. From the results obtained with the split and unsplit chrome tanned leathers, the following modifications were made in the testing procedure on the chrome retanned leathers. Since the water resistance data were so highly variable as to be of little value with regard to the selection for a suitable sampling location, only seven of these tests were made on each cow and steer. This permitted additional specimens for the bursting tests. The results for the chemical constituents were so highly uniform in the previous studies on split and unsplit leathers that the chemical analysis on only 4 cow sides and 4 steer sides was required for establishing a suitable sampling position.

Test Methods

The test methods used are described in Federal Specification KK-L-311, with a few exceptions which are described below. The strength, tensile, stitch tear, tongue tear, and burst tests were made on a Tinius Olsen Testing Machine [2], which by proper adjustment of the loading range afforded a high degree of precision at any required load. A special adapter was developed

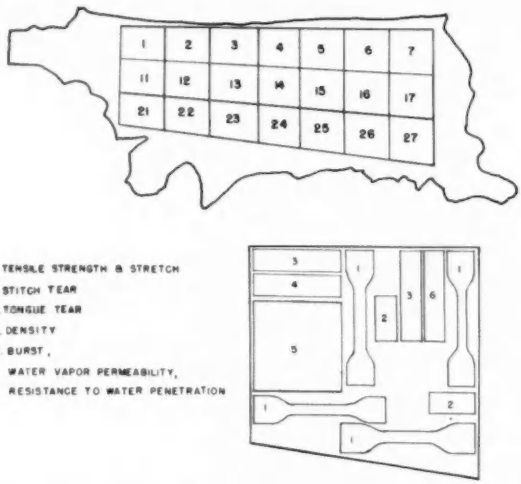

1 2 3 4 5 6 7
11 12 13 14 15 16 17
21 22 23 24 25 26 27
1. TENSILE STRENGTH & STRETCH
2. STITCH TEAR
3. TONGUE TEAR
4. DENSITY
5. BURST,
WATER VAPOR PERMEABILITY,
RESISTANCE TO WATER PENETRATION

FIGURE 1—Diagram showing side cut into blocks and a block cut into individual test specimens.

for use with this machine for measuring bursting strength. This apparatus was used instead of the standard Mullen tester because the latter did not have high enough capacity to break all of the side leather specimens in this experiment. This adapter was described in [1].

Results and Discussion

The detailed results of all the tests are presented in three separate papers [1, 4, 5]. The results given in this paper will be confined to those dealing directly with the problem of sampling and its application to specifications. Sampling positions for water resistance properties are not included in this paper because these properties are so variable that the selection of a location for sampling appears of little importance. The locations given in [1] for water penetration and water vapor permeability are probably sufficiently reliable.

Sampling Problem

The principal criterion used for the selection of the sampling location is the correlation coefficient between the results obtained for a particular test in a specific position (block) and the average result of that test for the entire side. This criterion and the fundamental considerations from which it was derived are fully described in [3].

TABLE 1
Part I

Correlation Coefficients
Side Averages vs Block Averages

Block Number	Tensile Strength								Stitch Tear							
	Split		Unsplit		Cows		Steers		Split		Unsplit		Cows		Steers	
	⊥	∥	⊥	∥	⊥	∥	⊥	∥	⊥	∥	⊥	∥	⊥	∥	⊥	∥
1	0.64	0.61	0.46	0.46	0.75	0.77	0.31	0.42	0.75	0.57	0.77	0.54	0.38	0.54	0.26	0.20
2	0.55	0.35	0.41	0.38	0.79	0.79	0.84	0.63	0.55	0.55	0.54	0.53	0.65	0.69	0.54	0.39
3	0.66	0.59	0.45	0.44	0.73	0.75	0.44	0.71	0.35	0.45	0.52	0.24	0.71	0.36	0.37	0.49
4	0.56	0.55	0.35	0.52	0.51	0.55	0.74	0.75	0.19	0.21	0.42	0.39	0.58	0.30	0.71	0.32
5	0.65	0.68	0.42	0.45	0.69	0.50	0.71	0.65	0.04	0.54	0.51	0.48	0.76	−0.05	0.68	−0.24
6	0.74	0.52	0.71	0.48	0.70	0.68	0.64	0.63	0.50	0.50	0.78	0.62	0.21	0.16	0.57	0.48
7	0.69	0.36	0.71	0.29	0.56	0.51	0.43	0.72	0.65	0.57	0.55	0.48	0.58	0.29	0.66	0.55
11	0.62	0.62	0.37	0.56	0.59	0.69	0.67	0.63	0.67	0.38	0.39	0.21	0.29	0.56	0.71	0.62
12	0.79	0.47	0.61	0.41	0.68	0.79	0.79	0.71	0.70	0.61	0.50	0.32	0.50	0.91	0.68	0.60
13	0.61	0.52	0.77	0.58	0.87	0.82	0.56	0.91	0.25	0.40	0.56	0.35	0.62	0.32	0.70	0.50
14	0.62	0.59	0.60	0.51	0.83	0.82	0.78	0.73	0.64	0.66	0.16	0.20	0.75	0.69	0.63	0.04
15	0.73	0.56	0.70	0.66	0.91	0.77	0.83	0.80	0.42	0.14	0.001	0.44	0.66	0.54	0.49	0.54
16	0.73	0.55	0.70	0.37	0.82	0.78	0.85	0.71	0.44	0.41	0.35	0.47	0.64	0.50	0.52	0.37
17	0.71	0.61	0.68	0.23	0.84	0.72	0.46	0.16	0.24	0.40	0.57	0.31	0.54	0.42	0.004	0.40
21	0.19	0.019	0.24	0.29	0.52	0.04	0.71	0.65	0.05	0.31	0.18	0.42	0.39	0.47	0.33	0.18
22	0.13	0.46	0.025	0.62	−0.20	0.31	0.40	0.16	0.00	0.004	0.40	0.42	0.68	0	0.36	0.38
23	0.66	0.29	0.32	0.56	0.59	0.05	0.63	0.51	0.64	0.29	0.40	0.11	0.21	0.09	0.42	0.30
24	0.56	0.52	0.57	0.42	0.77	0.63	0.65	0.75	0.48	0.10	0.44	0.14	0.35	−0.24	0.61	0.34
25	0.51	0.35	0.32	0.42	0.81	0.67	0.72	0.68	0.33	0.33	0.30	0.11	0.53	0.43	0.39	0.33
26	0.58	0.51	0.13	0.36	0.68	0.49	0.71	0.72	0.31	0.43	0.48	0.36	0.60	0.72	0.78	0.21
27	0.48	0.47	0.18	0.21	0.75	0.60	0.62	0.66	0.38	0.47	0.17	0.02	0.66	0.67	0.38	−0.18

TABLE I
Part II

Correlation Coefficients
Side Averages vs Block Averages

Block Number	Tongue Tear								Burst			
	Split		Unsplit		Cows		Steers					
	⊥	=	⊥	=	⊥	=	⊥	=	Split	Unsplit	Cows	Steers
1	0.33	0.51	0.64	0.72	0.64	0.08	0.64	0.64	0.71	0.61	0.80	0.46
2	0.54	0.40	0.57	0.52	0.91	0.14	0.58	0.47	0.56	0.67	0.80	0.66
3	0.15	0.40	0.69	0.66	0.26	0.41	0.44	0.59	0.58	0.77	0.65	0.62
4	0.33	0.45	0.58	0.63	0.55	0.70	0.56	0.39	0.33	0.73	0.59	0.68
5	0.69	0.56	0.69	0.57	0.61	-0.04	0.35	0.47	0.66	0.33	0.82	0.43
6	0.71	0.49	0.77	0.55	0.44	0.38	0.35	0.30	0.10	0.67	0.70	0.66
7	0.62	0.60	0.74	0.71	0.70	0.43	0.40	0.47	0.71	0.76	0.33	0.55
11	0.60	0.61	0.57	0.65	0.64	0.19	0.70	0.14	0.57	0.80	-0.15	0.34
12	0.83	0.69	0.69	0.84	0.63	0.65	0.42	0.49	0.55	0.59	0.55	0.76
13	0.27	0.72	0.63	0.81	0.84	0.23	0.82	0.86	0.63	0.47	0.76	0.66
14	0.41	0.64	0.49	0.62	0.62	0.87	0.48	0.38	0.79	0.77	0.61	0.62
15	0.44	0.65	0.69	0.34	0.64	0.48	0.40	0.38	0.75	0.72	0.84	0.65
16	0.77	0.55	0.56	0.56	0.59	0.59	0.11	0.51	0.74	0.37	0.60	0.40
17	0.47	0.65	0.69	0.57	0.45	0.23	0.29	0.53	0.70	0.81	0.66	0.69
21	0.33	0.31	0.33	0.39	0.31	0.51	0.28	0.56	0.22	0.23	-0.04	0.85
22	0.54	0.49	0.53	0.68	0.60	0.70	0.46	0.76	0.67	0.25	0.40	0.43
23	0.71	0.69	0.59	0.44	0.52	0.34	0.29	-0.05	0.28	0.67	0.45	0.46
24	0.75	0.51	0.47	0.60	0.59	0.45	0.54	0.28	0.33	0.28	0.55	0.36
25	0.40	0.53	0.67	0.50	0.67	0.37	0.56	0.40	0.53	0.35	0.32	0.49
26	0.58	0.61	0.42	0.65	0.56	0.29	0.19	0.06	0.32	0.15	0.56	0.11
27	0.57	0.60	0.79	0.68	0.39	0.49	0.40	0.65	0.57	0.19	0.74	0.54

Correlation coefficients for side averages with block averages for tensile strength, stitch tear, and tongue tear, in two directions of test, and for burst are given in Table 1. As shown by Table 2, the correlation coefficients for tensile strength are generally higher in the perpendicular direction of test. The agreement between the correlation coefficients for the four sets of sides is illustrated in Figure 2 for tensile strength in the perpendicular direction. On the average, the positions in the belly row show considerably lower correlation with side average than those in the other two rows. Moreover, the correlation coefficients in the belly row are much less consistent between the four groups of sides.

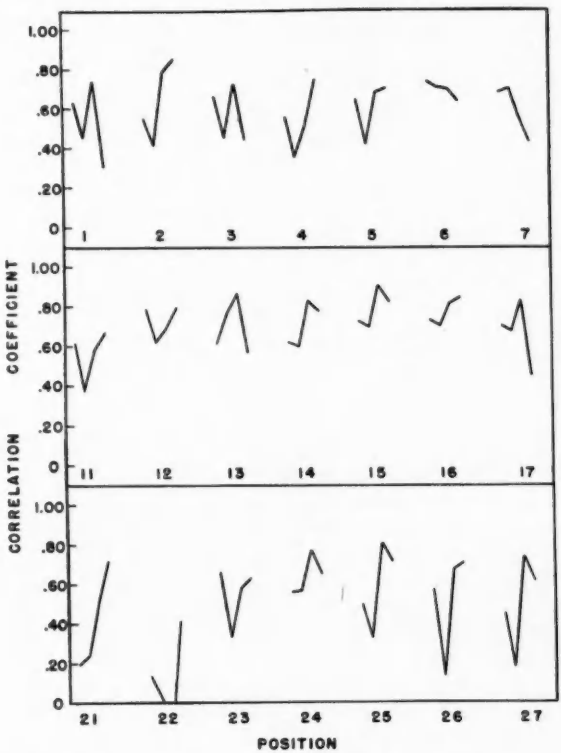


FIGURE 2—Coefficients of correlation for tensile strength, in perpendicular direction, of position vs. side averages. Results at each position are plotted in the following order: (1) split chrome steer side leather, (2) unsplit chrome steer side leather, (3) chrome retanned cow side leather, and (4) chrome retanned steer side leather.

TABLE 2

Direction Having Highest Correlation Coefficient for Tensile Stregnth

Position	Split	Unsplit	Cows	Steers
1	+	0	–	–
2	+	+	0	+
3	+	+	–	–
4	+	–	–	–
5	–	–	+	+
6	+	+	+	+
7	+	+	+	–
11	0	–	–	+
12	+	+	–	+
13	+	+	+	–
14	+	+	+	+
15	+	+	+	+
16	+	+	+	+
17	+	+	+	+
21	0	–	+	+
22	–	–	–	+
23	+	–	+	+
24	+	+	+	–
25	+	–	+	+
26	+	–	+	–
27	+	–	+	–

+ = perpendicular direction highest
– = parallel direction highest
O = no difference

Ranking of Sampling Positions

The experiments described have permitted the calculation of a correlation coefficient for each test in each position. However, this coefficient is merely an estimate of the true coefficient and will vary from experiment to experiment. Furthermore, in combining the results for the four different sets of sides, it must be remembered that the results with the cow and steer sides were based on 15 sides, whereas the others were based on 30 sides. In comparing positions on the basis of these observed coefficients of correlation, account must be taken of the sampling fluctuations of these estimates. This can be done most effectively by grouping the correlation coefficients for any given property into a number of groups such that within each group the differences would not be considered statistically significant, while the differences between successive group averages are significant. The grouping procedure is explained in detail in the paper [3] on the development of the theoretical basis of the statistical solution of this sampling problem. It is shown there that the correlation coefficients must be converted into "Z-values", which are then grouped in "Z-intervals".

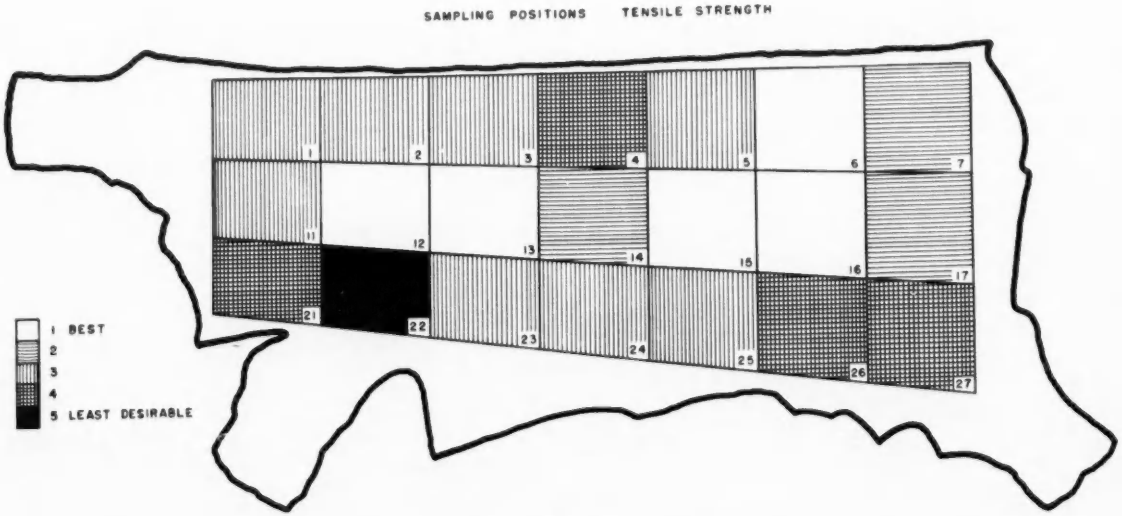


FIGURE 3—Evaluation of blocks as sampling positions for tensile strength test.

TABLE 3

Grouping According to Z-Intervals

Z-interval	Limits for range of Z		Limits for range of r	
	Lower	Upper	Lower	Upper
0	2.57	2.65	0.99	0.99
1	2.42	2.56	0.99	0.99
2	2.27	2.41	0.98	0.99
3	2.11	2.26	0.97	0.98
4	1.96	2.10	0.96	0.97
5	1.81	1.95	0.95	0.95
6	1.66	1.80	0.93	0.94
7	1.50	1.65	0.91	0.92
8	1.35	1.49	0.87	0.91
9	1.20	1.34	0.83	0.87
10	1.05	1.19	0.78	0.83
11	0.89	1.04	0.71	0.77
12	0.74	0.88	0.63	0.70
13	0.59	0.73	0.53	0.62
14	0.44	0.58	0.41	0.52
15	0.24	0.43	0.24	0.40
16	0.00	0.33	0.00	0.32

The standard deviation of Z is equal to $1/\sqrt{}$ N-3 and for four sets totaling 90 sides becomes $\sigma = 1/\sqrt{}\ 90\text{-}12 = 0.11$. In the theoretical paper[3], reasons are given for spacing the midpoints of successive Z-intervals 2x0.675 standard deviations apart, i. e., 2 x 0.675 x 0.11 units apart in this instance. The Z-intervals are shown in Table 3. The corresponding results obtained on this basis for the four physical tests – tensile strength, bursting strength, stitch tear, and tongue tear - are given in Table 4 and graphs of the results for tensile strength, bursting strength, and stitch tearing strength are given in Figures 3, 4, and 5, respectively. Z-intervals 14 and 15 are combined in the figures to give one less group than that shown in the tables.

The best sampling positions shown in Table 4 for each physical test may be used in research work where the best possible location for each test might be desired. However, for acceptance testing or for other tests where it is desired to save as much leather as possible, it may be expedient to make all tests in one position. For this purpose the ratings for each position shown in Table 4 for each test have been averaged and ranked. The results shown in Table 5 and Figure 6 are the ranking of the positions if all tests are to be made in the same one. Figure 6 gives 6 groupings of the locations. The locations in each group have approximately equal rank. Locations 12 and 7 have the highest rank. Since location 7 can be located more accurately, and since it is on the edge of the side, thus simplifying the cutting procedure, it has been selected as the location which should be used for sampling for acceptance testing.

TABLE 4

Arrangement of Blocks According to Z Ranges and the Number of Sides Which Must be Sampled to Show 10 Percent Difference Between Lots With a Degree of Confidence of 90 Percent

Z-interval	Z-range	Block Number	No. of Sides
	Bursting Strength		
11	0.89—1.04	15, 14, 17	22
12	0.74—0.88	3, 1, 7, 2	27
13	0.59—0.73	13, 12, 4, 11, 5, 16	39
14	0.44—0.58	6, 23, 27, 22, 25	55
15	0.34—0.43	24, 21	88
16	0—0.33	26	209
	Tensile Strength		
11	0.89—1.04	15, 16, 12, 13, 6	22
12	0.74—0.88	17, 14, 7	26
13	0.59—0.73	2, 24, 5, 3, 1, 11, 25, 23	35
14	0.44—0.58	4, 26, 27	53
15	0.34—0.43	21	86
16	0—0.33	22	204
	Stitch Tearing Strength		
12	0.74—0.88	1	18
13	0.59—0.73	7, 12, 6, 2, 11	24
14	0.44—0.58	14, 26, 13, 3, 23, 24, 16, 5, 4	36
15	0.34—0.43	17, 25, 27, 15	58
16	0—0.33	22, 21	137
	Tongue Tearing Strength		
11	0.89—1.04	12	28
12	0.74—0.88	6, 7, 2, 5	34
13	0.59—0.73	13, 27, 24, 11, 16, 23, 25, 15, 1, 17, 22	45
14	0.44—0.58	4, 14, 26, 3	68
15	0.34—0.43	——	—
16	0—0.33	21	262

Sampling for Chemical Tests

The results of the tests given in [1] indicate that the chemical constituents do not vary nearly as much as the results of the physical property tests. The studies given in that paper further indicate that reliable results may be obtained in nearly every position using only a few sides. A very convenient arrangement from the standpoint of the saving of leather is to use the same position for the chemical tests as is used for the physical tests. Location 7 should therefore be used for the chemical tests.

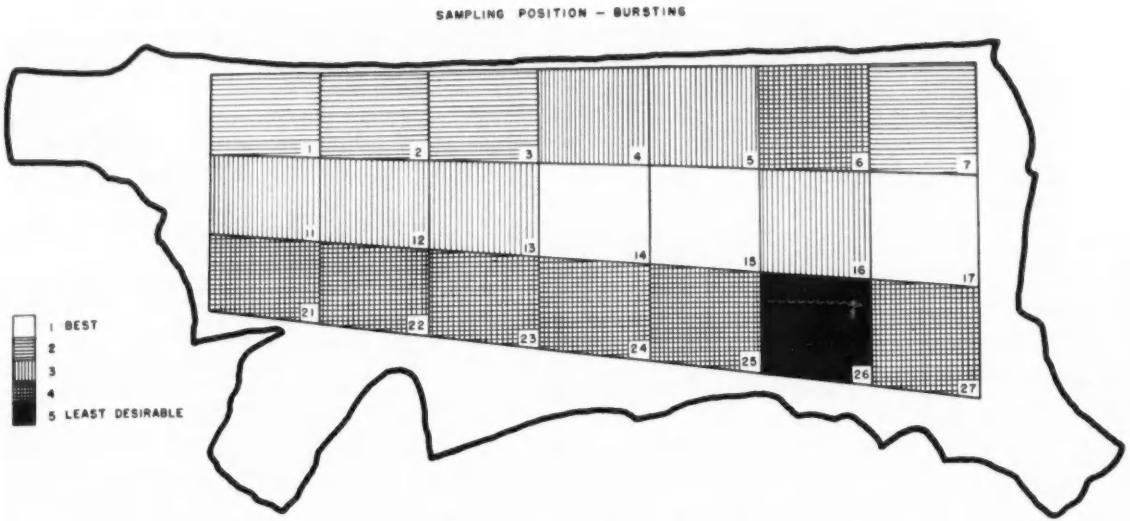


FIGURE 4—Evaluation of blocks as sampling positions for bursting test.

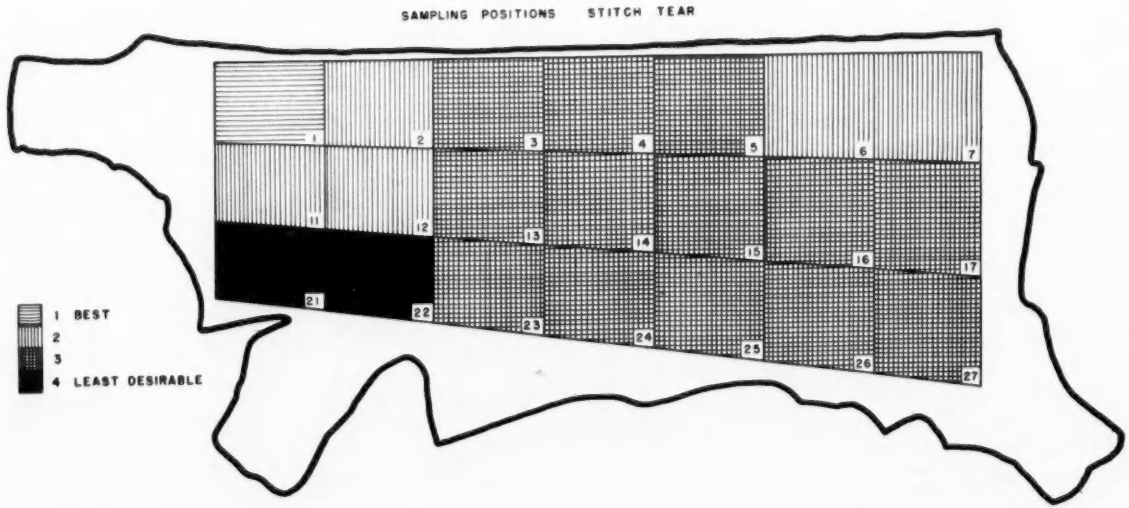


FIGURE 5—Evaluation of blocks as sampling positions for stitch tear test.

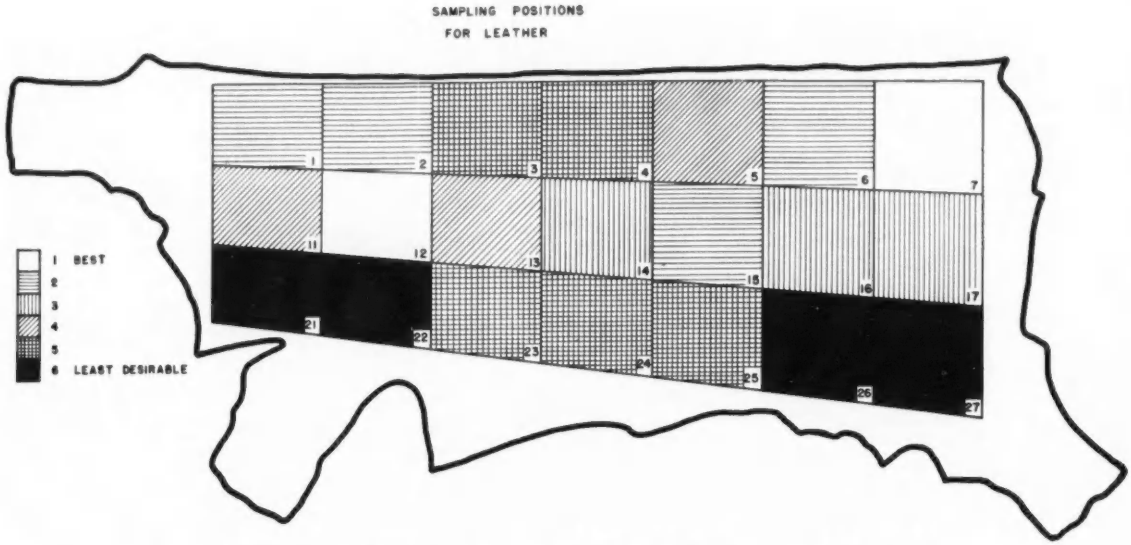


FIGURE 6—Evaluation of blocks as sampling positions if all tests are made in same block.

TABLE 5

Ranking of Sampling Locations
(Burst, stitch tear, tensile, and tongue tear made in same block)

Rank*	Block No.
1	12
2	7
4.5	1, 2, 6, 15
8	14, 16, 17
11	5, 11, 13
13	3
14	23
16	4, 24, 25
18	27
19	26
20	22
21	21

*1—best 21 — poorest

The ranking of the positions for the testing for hide substance is given in Table 6 and Figure 7. These data were taken from the results obtained from the testing of the 30 split chrome tanned sides. Because of the low variability of the chemical results from these sides, it was not deemed necessary to make further detailed analyses other than those made on these first 30 sides. Position 7 is ranked in the highest group of locations for the hide substance determination.

TABLE 6

Ranking of Positions for Hide Substance Determination and Number of Sides Required for Detection of 10 Per Cent Difference with a Degree of Confidence of 90 per Cent.

*Z-interval	Z-range	Block numbers	Number of Sides
4	0.89—1.27	17, 21, 23, 7, 5, 6	3
5	0.76—0.88	26, 12, 3, 15, 27, 22, 24	4
6	0—0.75	16, 11, 25, 4, 14, 1, 13, 2	10

*See reference (1) for corresponding r-range.

Calculation of Sample Size

In the comparison of two lots for a particular property, it is important to know how many sides should be taken from each lot in order to detect with a given degree of confidence the minimum difference in which one is interested. It is assumed that the property is measured on each side in the same position, P, or group of positions for which the coefficient of correlation, r, is known.

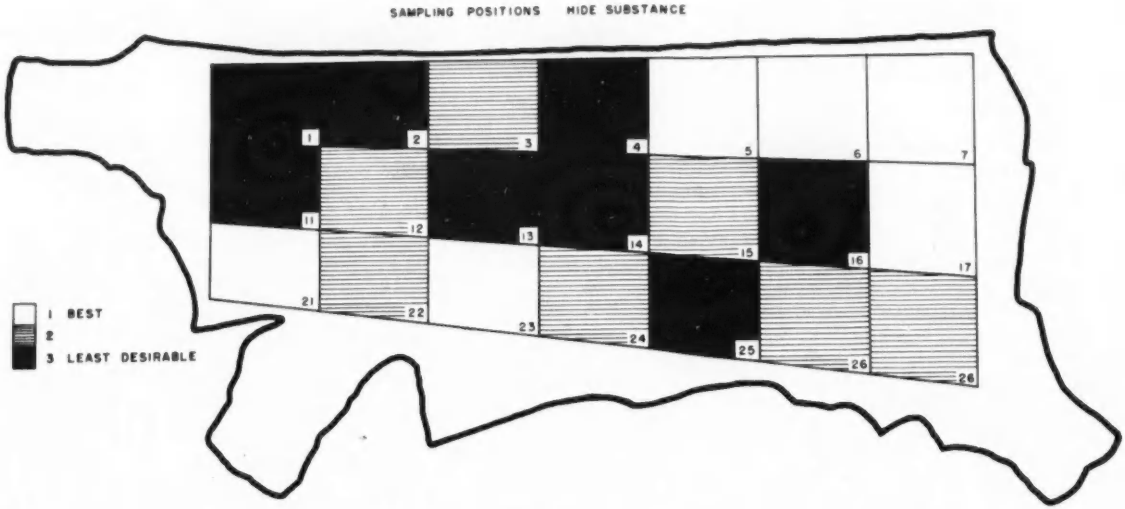


FIGURE 7—Evaluation of blocks as sampling positions for determination of hide substance.

The calculation for sample size may be made with the following formula derived in [3]:

$$N = K\frac{V^2}{r^2 D^2}$$

where N is the number of sides, V is the coefficient of variation in per cent characterizing the side-to-side variability within each lot for the property under consideration. The factor K depends on the degree of confidence required for the detection of the per cent difference, D. The number of sides required for the detection of 10 per cent difference with a degree of confidence of 90 per cent is given for each group of positions ranked according to Z in Tables 4 and 6.

The side-to-side variability within the lot for the four principal physical tests and for hide substance is given in Table 7. Results for tensile strength and stitch and tongue tearing strength are given for the perpendicular direction. These values are averages for the four different sets of sides, namely – chrome tanned split and unsplit, and chrome retanned cow and steer sides.

TABLE 7

Side to Side Variability Within the Lot

	Coefficient of variation
	Per cent
Tensile strength	8.3
Stitch tear	6.8
Tongue tear	9.4
Burst	8.4
Hide substance	3.0

Setting of Specification Limits

An application resulting from the determination of the best sampling location for the evaluation of upper leather, is the setting of minimum requirements for specification purposes. As an illustration, a procedure used for setting the requirement for tensile strength will be shown. For retanned upper leather there are available the data from the cow sides and the steer sides. Since the cow sides showed the highest coefficient of variation in location 7, which is the sampling location, the data from these were chosen.

It is generally assumed in the leather industry that leather having a tensile strength of less than 1800 psi is too weak to be satisfactory for shoes. A tensile strength of about 1800 psi should therefore be the minimum average value in any part of the hide. From the data [5] on the cow sides, it was noted that the average value for tensile strength in position 7 was 3210 pounds and in position 1 where the strength was the lowest it was 1990 pounds. Thus, from the

ratio

$$\frac{X}{1800} = \frac{3210}{1990}$$

X = 2900. Position 7 must have an average value of 2900 psi to assure that the average value in position 1 will not fall below 1800 psi.

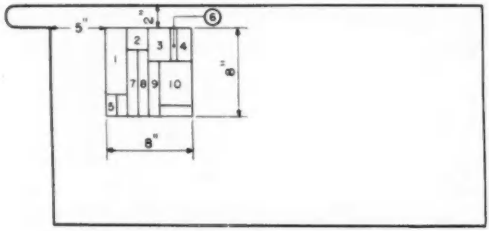
The value 2900 is an average, and in order to assure within a certain degree of confidence that no value falls below this figure, an additional factor must be applied. This factor is based on the coefficient of variation in position 7, the value of which was found to be 17.1%[1], and on the number of sides sampled. The minimum limit based on a sample of 15 sides with a confidence of 97.5 per cent will be

$$2900 + 2 \times \frac{0.171 \times 2900}{15} = 3156 \text{ psi.}$$

Recommended Procedure for Acceptance Testing

From the results of these studies the following procedure is recommended for acceptance on specification testing. Since position 7 was found to be the best sampling location if all tests are to be made in one position, it is recommended not only for upper leather but for other types of leather, such as sole leather and mechanical leathers or wherever sampling is done on a side or a part threof containing position 7.

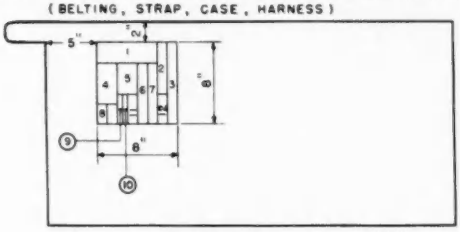
PROCEDURE FOR CUTTING PIECES FOR TESTS ON SOLE LEATHER



NO	DIMENSIONS OF PIECE INCHES	TEST
1	2 × 6	TENSILE
2	2 × 2	COMPRESSIBILITY
3	2 × 3	CHEMICAL
4	1½ × 3	WATER ABSORPTION
5	1 × 2	STITCH TEAR
6	½ × 3	SHRINKAGE TEMP
7	1 × 6	CROCKING
8	1 × 6	PIPING
9	1 × 5	STIFFNESS
10	3 × 4	WATER VAPOR PERMEABILITY

FIGURE 8—Diagram of tentative procedure for cutting specimens for acceptance testing of sole leather.

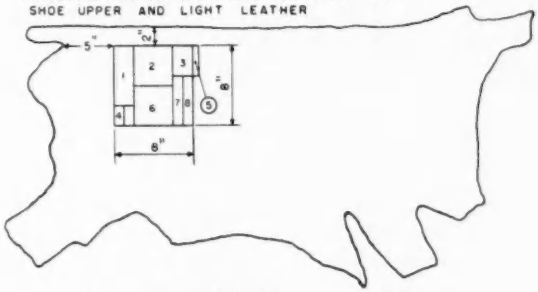
PROCEDURE FOR CUTTING PIECES FOR TESTS ON MECHANICAL LEATHER
(BELTING, STRAP, CASE, HARNESS)



NO	DIMENSIONS OF PIECE INCHES	TEST
1	2 × 6	TENSILE
2	1 × 5	TONGUE TEAR
3	1 × 8	BUCKLE TEAR
4	2 × 4	WATER ABSORPTION
5	2 × 3	CHEMICAL
6	1 × 6	CRACKINESS
7	1 × 6	PIPING
8	1 × 2	STITCH TEAR
9	½ × 3	SHRINKAGE TEMP
10	½ × 3	STIFFNESS
11	1 × 3	TACKINESS
12	1 × 3	CROCKING

FIGURE 9—Diagram of tentative procedure for cutting specimens for acceptance testing of mechanical leathers.

PROCEDURE FOR CUTTING PIECES FOR TESTS ON SHOE UPPER AND LIGHT LEATHER



NO	DIMENSION OF PIECE INCHES	TEST
1	2 × 6	TENSILE
2	4 × 4	BURST
3	2 × 3	CHEMICAL
4	1 × 2	STITCH TEAR
5	½ × 3	SHRINKAGE TEMP
6	4 × 4	WATER ABSORPTION, WATER PENET., WATER VAPOR PERMEABILITY
7	1 × 5	TONGUE TEAR
8	1 × 5	STIFFNESS

FIGURE 10—Diagram of tentative procedure for cutting specimens for acceptance testing of shoe upper and light leathers.

Sketches giving the proposed position and directions for cutting pieces for the physical and chemical tests for sole leather, mechanical leather, and upper leather, are given in Figures 8, 9, and 10, respectively. Only those pieces specified for tests in the specification will be used. The figures include pieces for some tests which are not required in most specifications at the present time.

It is proposed that 15 units of sides or bends, etc. be sampled from each lot containing more than 15. For lots containing 15 or fewer units, it is proposed that each unit be sampled.

Conclusions

A procedure for the sampling of side upper leather has now been firmly established with additional studies on unsplit chrome tanned leather and split chrome retanned cow and steer sides to supplement those obtained with split chrome tanned leather [1]. The results with the 3 different lots of leather mentioned are in close agreement with those obtained with the lot of split chrome tanned leather. Position 7 proved to be a good location for all tests applied to the split chrome tanned lot. Positions 21 and 22 and others in the belly were found to be poor positions, which also agrees with the results obtained with the last 3 lots of leather studied. The influence of direction of test on the results is similar for the 4 different lots studied as is also the high variability of the physical properties and the comparatively low variability of the chemical constituents. The agreement in the magnitude and variation of the physical properties as a function of hide position for the 4 lots indicates that these properties are inherent in the basic fiber structure of the hide and are not critically influenced by the tanning process. The principle of establishing a uniform position for the sampling of all types of leather is therefore fundamentally sound.

References

1. Mann, C. W., Randall, E. B., Mandel, John, Kilduff, T. J., and Charles, A. M., *J. Am. Leather Chem., Assn.* **46,** 248 (1951).
2. Tinius Olsen Testing Machine Co., Easton Rd., Willow Grove, Pa.
3. Mandel, John and Mann, C. W., *J. Research NBS*, **46,** 99 (1951), RP2180.
4. Randall, E. B., Carter, T. J., Kilduff, T. J., Mann, C. W., and Kanagy, J. R., "The Variations of the Physical and Chemical Properties of Split and Unsplit Chrome Tanned Leathers". Not yet published.
5. Kanagy, J. R., Randall, E. B., Carter, T. J., Kinmonth, R. H., and Mann, C. W., "Variation of Physical and Chemical Properties Within and Between Vegetable Retanned Cow and Steer Sides." Not yet published.

Received March 14, 1952.

BOOK NOTICES

Quantitative Organic Microanalysis. Al. Steyermark. XII, 389 pages. The Blakiston Co., 1012 Walnut St., Philadelphia 5, Pa. 1951. $7.00. The procedures described in this book are those that have been used in the author's laboratory for the past decade and are known to give reliable results. Usually only one procedure is described for each determination, but brief references to other procedures are given and an extensive bibliography is included at the end of each chapter. Excellent dimensioned line drawings of apparatus are also included. A chapter is devoted to each of the following determinations: metals by the ashing technique, nitrogen by the micro Dumas method, carbon and hydrogen, nitrogen by the Kjeldahl method, sulfur, halogens, phosphorus, arsenic, oxygen, neutralization equivalent, alkoxyl groups, and acetyl groups. In addition there are chapters on each of the following subjects: introduction, the microchemical balance, weighing on the microchemical balance, preparation of samples for analysis, standard solutions, determinations carried out on the Van Slyke manometric apparatus, determination of molecular weight, other determinations, determination of some physical constants, and calculations. In the chapters on elemental and group analysis the methods are those adopted by the Association of Official Agricultural Chemists and the apparatus is that recommended by the American Chemical Society's Committee for Standardization of Microchemical Apparatus on which the author has served as chairman. The paper, printing and binding are satisfactory. R. S. A.

Basic Organic Chemistry. By J. R. Schwenck and R. M. Martin. Cloth, 323 pages. Published by The Blakiston Co., Philadelphia, Pa. 1951. Price $4.50. The authors made it plain that their objective was to write a book which would so simplify an exceedingly complex subject that it could serve as the basis for a one semester course, designed to give the student sufficient knowledge of organic chemistry to make it understandable as an aid and adjunct in such neighboring fields as medicine, agriculture, chemical engineering and home economics. In order to accomplish this objective they have tried to avoid, as far as possible, the principal causes of confusion for the beginner. Particularly, they attempted to overcome the confusion due to scrambled nomenclature, which they term acute "nomenclaturitis", and lack of a logical correlation with the principles of general chemistry. To overcome the former they stick religiously to I.U.C. nomenclature throughout but, after the student has become familiar with it, they devote an entire chapter to the subject of nomenclature, thus preparing the student for the confusion of names he will certainly encounter. Since the book has only twenty chapters, this is an unusual but entirely justifiable emphasis on this phase of the study. To correlate organic with general chemistry, the electronic approach is used throughout. In general the subject matter is developed along classical lines, beginning with carbon thence to the final heterocylclic ring compounds via the usual route of hydrocarbons, halogenated compounds, oxygen containing compounds, etc. The treatment of heterocyclic compounds is somewhat unusual because of laying the emphasis on the similarities of these compounds with those previously studied rather than upon the dissimilarities. This undeniably does help in the assimilation of this group into the corporate body of the science. At the end of most chapters, reaction summaries in tabular form do much to fix the relationships for the student.

The last three chapters are devoted to the industrial, biological and military aspects designed to give those, primarily interested in other fields, a speaking acquaintance with the major developments in commerce, war and everyday living based essentially on organic chemistry. The book fulfills well the aims of the authors and accomplishes equally well an objective which they perhaps did not foresee. It is a fact that progress in all fields is so rapid that only the specialists in any subject can keep fully abreast. This is particularly true for the practical chemist, who is so taken up with the immediate economic application

that he has little time for the theoretical backgrouund. Yet the time inevitably comes when some sort of catching up and tieing of loose threads is necessary. The practical leather chemist will find this an excellent book for that purpose in organic chemistry. R. H. T.

ABSTRACTS

The Pressure Baling of Line Dried East African Goat Skins with Reference to Cracking. By J. R. Furlong. *Colonial Plant and Animal Products*, **2**, 23 (1951). The investigation in question was undertaken to determine whether goat skins which had been dried over a line, and in consequence given a folding along the back bone, suffered any damage by cracking when baled under pressure by the method normally used in East Africa. Three lots of skins, prepared in Uganda, consisting of 2,000 skins each, were baled under hydraulic pressure at Mombassa and shipped to three tanneries in the United Kingdom. The first lot of skins showed no cracking on examination in the raw state. After liming, 175 skins showed putrefactive damage, some of which occurred along the back bone. No change due to baling was observed. The reports on the second and third lots of skins were similar to the first. It was concluded that pressure baling under the conditions described does not cause the skins to crack. Since putrefactive damage was found throughout the skins, the cause is attributed to delay between flay and cure.

Suspension Dried Hides from Batsutoland. By J. R. Furlong. *Colonial Plant and Animal Products*, **2**, 25 (1951). In connection with efforts being made to improve hides from Batsutoland, 64 suspension dried hides were shipped to England for tanning trials. The report on them showed that there was some take-off damage but on the whole it was not bad. The drying was well carried out as there was no putrefaction damage. They were approximately equal in quality to the best suspension dried hides from East Africa as regards substance and preparation, but were lower in grain quality.

New pH Standards. *J. Franklin Institute*, **250**, 554 (1950). The Bureau of Standards has selected four new standards to provide fixed points at the upper and lower ends of a standard pH scale. These are as follows: (1) A mixture of sodium bicarbonate and sodium carbonate, both at 0.025 molar concentration, with a pH of about 10 at room temperature. (2) A 0.01 molar solution of trisodium phosphate, pH about 11.7. (3) A solution of potassium hydrogen tartrate saturated at room temperature, pH about 3.6. (4) A 0.01 molar solution of potassium tetroxalate, pH about 2.1.

Dyeing of Chrome Leather with Anionic Dyes. By G. Otto. *Melliand Textilber.*, **32**, 311 (1951). Through *J. Soc. Dyers and Colourists*, **67**, 354 (1951). Modern theories of chrome leather dyeing with acid and direct dyes are reviewed. Experiments are described comparing uptake of acid and direct dyes by columns of collagen fibers, electrolyte-free chromic hydroxide, and chrome leather. It was found that increase in molecule size and number of chromophoric groups in the molecule of anionic dyes resulted in increased affinity between the dye and the chrome leather. This serves to explain the observation that, when chrome leather is retanned with vegetable tannins and is subsequently dyed with anionic dyes, those dyes which exhibit high affinity for pure chrome leather now show just as low affinity as dyes of low molecular weight. It is also possible to explain the effect of drying leather on its subsequent affinity for dyes.

Quality Controlling Leather. By E. R. Theis, *Lea. and Shoes*, **122,** No. 22, 10 (1951). It is recommended that leather samples be cut into 8 to 10 layers and each analyzed separately if a comprehensive knowledge of the product is to be obtained. Stratigraphic analysis is regarded as a means of process control and leather evaluation which is far superior to whole piece analysis.

Furans for Processing Leather. By T. A. Dickinson. *Lea. and Shoes*, **122,** No. 23, 14 (1951). There are indications that furan plastic resins can be used to supplement or replace other types of natural or synthetic materials as impregnants, coatings and adhesives for leather. Their inherent dark color has limited their general use heretofore. The furans have many desirable and physical qualifications—properties that cannot be equalled by some of the resins now most extensively used by leather manufacturers. When polymerized, they have more mechanical strength than many used thermosets. They can be compounded for use as thermosetting or thermoplastic resins of maximum or minimum flexibility after polymerization. Typical furans are phenol-furfural, furfural-lignin and furfural-alcohol resins. They are available as liquid monomers, dispersions and emulsions. Monomeric furans are obtainable as low viscosity solutions, with no volatile constituents. As such they can penetrate porous materials. Cowhide leather strips impregnated with one of these resins, and heated for 10 hours with infrared light, had increased rigidity but retained some flexibility. Furfurylated dimethylolurea coatings are excellent leather adhesives. Pigmented dispersions of the foregoing resin are suitable for finishing leather surfaces, making them more water impervious and abrasion resistant.

A Suggested Program for Industry Sponsored Shoe Research. By R. B. Hobbs *Lea. and Shoes*, **123,** No. 1, 8 (1952). The author outlines an organizational program for shoe research. Such problems as (a) prevention and cure of trouble connected with materials, processes and products; (b) reduction of costs of materials, processes and products; (c) improvement in manufacturing techniques, and in quality of materials and products; (d) development of new materials and processes, and of emergency alternates when shortages occur; (e) increase of technical knowledge leading to better understanding of materials, processes and products; and (f) contribution to the common store of fundamental scientific information, should be considered. Three types of research are proposed, namely: applied research and development, technical service to sponsors, and fundamental research. The research institute should have three divisions, such as physics and engineering, physiology, and management techniques. The author discusses his proposal from the cost, financial support and location basis, and advocates the prompt publication of the institute's findings.

Vacuum Impregnated Leathers. By T. A. Dickinson. *Lea. and Shoes*, **123,** No. 2, 12 (1952). Vacuum impregnation of leather is claimed to reduce processing time, secure better penetration of the impregnants, and reduce plant space for a given output. Heretofore high vacuum pumps were not available but as of now this deficiency has been overcome, thus making high vacuum impregnation commercially feasible.

The Physical Testing of Leather. By W. T. Roddy, *Shoe and Lea. Reporter*, **263,** No. 13, 12 (1951). The author describes the several physical tests for leather and stresses their importance in its evaluation.

***Alchornea Cardifolia* Leaves and Bark from Nigeria.** By H. Bennett. *Colonial Plant and Animal Products*, **1**, 132 (1950). The leaves and bark of *Alchornea cordifolia* from Nigeria contains 10 and 11 per cent tannin. Non tannin extractables were 12 and 8 per cent, hence the high ratio of nontannin to tannin precludes the commercial exploitation of this material.

Leather Tanning with Natural and Synthetic Materials. By E. Nobili. *Boll. Staz. sper. Industr. Pelli Mater. concianti*, **26**, 205 (1950). Through *Brit. Abstr.*, BII, 458 (1951). Advantages of mixed natural and synthetic tanning agents are: decreased astringency and increased speed of penetration into the leather, grain-free leathers, reduced formation of insoluble matter and increased efficacy of extracts and clearer colors and greater resistance to climatic changes. Possible mechanisms for the action of artificial tanning agents are suggested.

Advantages and Disadvantages of Marked Chrome Salts for Tanning Box and Suede Leathers. *Boll. Staz. sper. Industr. Pelli Mater. concianti*, **26**, 189 (1950). Through *Brit. Abstr.*, BII, 459 (1951). The affinity of leather for dyes is very much controlled by the nature of the tanning agent. The stabilization of anionic chrome complexes attached to the leather diminishes the affinity for anionic dyes. As pH changes from 3.5 to 6.5, the absorption of dye changes from 98 to 47 per cent for Orange II, and 0 to 28 per cent for Methyl-violet B with leather tanned in chrome sulfite complex. The corresponding figures for leather tanned in tetra-oxalato-dihydroxychromiate are 15 to 0 per cent and 58 to 93 per cent; while for chrome sulfate tanned leather they are 99 to 88 per cent, and 0 (at all pH values). Chrome sulphthalate appears to be a useful tanning agent.

Methylglyoxal as a Tanning Agent. By K. H. Gustavson, *Svensk Kem. Tidskr.*, **59**, 159 (1947). Through *Brit. Abstr.* BII, 538 (1951). Data on the irreversible fixation of methylglyoxal by hide powder, the inactivation of acid binding protein groups of collagen, the degree of tryptic digestion, and the raised shrinkage temperature of collagen treated with methylglyoxal indicate that its tanning effect is about equal to that of formaldehyde but greater than glyoxal. As methylglyoxal is now available commercially, its employment as a technical tannning agent is suggested. The possibility of protein hardening by methylglyoxal occurring in some biological systems is considered.

A Backward Glance at Technical Research for Leather. By F. O'Flaherty, *Shoe and Lea. Reporter*, **264**, No. 13, 57 (1951). A review of research accomplishments in hide, leather and tanning materials.

Materials Handling and Equipment Efficiency in the Tannery. By F. E. Rueping. *Shoe and Lea. Reporter*, **264**, No. 11, 22 (1951). Mechanical transportation, well planned production flow, efficient utilization of equipment, and unit machine motorization are given as means of reducing costs and improving labor relations in the tannery.

New Fungicides for Leather. *Chem. Age*, **63**, 875 (1950). (1) Through *Brit. Abstr.* BII, 459 (1951). Advantages and disadvantages of some recently introduced fungicides for the treatment of leather are described.

Secondary Reactions in the Stabilization of Collagen by Hexathiocyanato-Chromiate. By K. H. Gustavson. *Svensk Kem. Tidskr.*, **62,** 165 (1950). Through *Brit. Abstr.* BII, 610 (1951). $K_3Cr(CNS)_6$ was prepared by the original method of Roesler whereby all the chromium is anionic. Samples of calfskin, hide powder, cod skin, and heat denatured hide powder were treated with the above aqueous chrome compound (10 per cent). Acetone dehydrated pelt and hide powder were also treated with an alcoholic solution of $K_3Cr(CNS)_6$. The irreversible fixation of hexathiocyanato-chromiate by collagen depends on the previous treatment of the latter, indicating that the attachment of the Cr is by coordination to the peptide linkings. Chrome fixation by collagen from nonaqueous solution is only 40-50 per cent of that from the aqueous system. The additional chrome fixation from aqueous solution is due to a gradual hydrolysis to form more active tanning compounds with the removal of the CNS groups. Cod skin and hide powder fix much more chrome than does calfskin. The $K_3Cr(CNS)_6$ tanned pelt is resistant to the action of trypsin. Hide powder tanned with $K_3Cr(CNS)_6$ and washed free from soluble chrome with ethyl alcohol fixes sulfur and chrome in the proportions present in $K_3Cr(CNS)_6$, but the collagen was not tanned. The shrinkage temperature was not raised unless the $K_3Cr(CNS)_6$ treated pelt was only slowly raised to the shrinkage temperature. In these circumstances, hydrolysis of the $K_3Cr(CNS)_6$ occurs to form a chrome tanning compound of greater tanning properties. The reaction of the hexa compounds with collagen is facilitated by exposure to daylight.

Depilatory Action of Barium Sulfide. By J. Criscuolo. *Boll. Staz. sper. Industr. Pelli. Mater. concianti,* **27,** 24 (1951). Through *Brit. Abstr.*, BII, 611 (1951). The hair swelling properties of barium sulfide are much less drastic than those of equivalent amounts of sodium sulfide, but it is not always possible to substitute barium sulfide for sodium sulfide in commercial unhairing preparations.

Chrome and Iron in Tanning Extracts. By G. A. Bravo, *Boll. Staz. sper. Industr. Pelli Mater. concianti,* **27,** 3 (1951). The copper content of tanning extracts is very low, being only 0.4 mg. per 100 g. in chestnut bark extract. Its effects on tanning are negligible. Details are given of its colorimetric estimation by the blue color with ammonia. Bark extracts contain much more iron, the average being 4-5 mg., although sometimes it is as high as 20 mg. per 100 g. Even these amounts do not have much effect on the color of leather. Estimation is best done colorimetrically by potassium thiocyanate.

Brazilian Sole Leathers. By L. Anusz. *Rev. Quim. industr., Rio de Janeiro,* **19,** No. 218, 16 (1950). Through *Brit. Abstr.* BII, 706 (1951). An analysis has been made of 12 samples of Brazilian sole leather, eleven of which were tanned with black acacia or a mixture of acacia and a little quebracho, and one with quebracho alone, and one foreign leather. In all of the eleven samples in which black acacia was used, the degree of tanning, as measured by the ratio of combined tannin to hide substance, was low, and the leather was soft.

Dyeing of Leather. By A. Simoncini. *Boll. Staz. sper. Industr. Pelli, Mater. concianti,* **27,** 42 (1951). A discussion of the types of dyestuffs used for leather, with details of the differences in their chemical nature and method of application.

Ultravon W in Fatliquoring. By M. Schwank. *Ciba Rev.* No. 84, 3064 (1951). Through *Brit. Abstr., BII,* 706 (1951). Addition of 0.1–0.2 per cent of Ultravon W to fat-

liquoring emulsions stabilizes them, assists them to penetrate leather, and most importantly keeps the precipitated lime soaps finely dispersed and so prevents them from blocking the pores of the leather. No further clearing process, such as rubbing with lactic acid, is then necessary before finishing with Capaderm colors.

Mechanism of Mineral Tanning. By T. Schachowskoy. *Melliand Textilber.* **32,** 302 (1951). Through *Brit. Abstr., BII,* 796 (1951). The following aspects of mineral tanning are discussed: Structure of collagen and its relation to that of animal and polyamide fibers, mechanism of the weighting of natural silk with tin compounds, the influence of neutralization on the absorption of chrome salts by pelts, the affinity of collagen and chrome leather for acids, the application of spectrophotometrical methods and the use of gelatin as a model substance for the study of mineral tanning phenomena, tanning with cobalt and other metal compounds, and decomposition and fixation of chrome tannins in pelts. Many analogies are drawn between operations of leather processing and textile finishing.

True Green Weight of Hides. By E. Simoncini. *Boll. Staz. sper. Industr. Pelli, Mater. concianti,* **27,** 71 (1951). Through *Brit. Abstr., BII,* 943 (1951). The dehydrating action of curing salts renders difficult the obtaining of the weight of the hide of a freshly killed animal from the weight of the treated hide. Soaking of the dried hide with water at 1.2° causes a 15 per cent recovery of weight and 7 per cent when water at 21° is used. Making temperature corrections in this way, the green weight of a skin may be calculated from the dry weight to within one per cent, without the soaking process. An apparatus is described for the determination of d of fresh skins, and this is found to be 1.104. The reduction in volume on treatment with curing salts is due to dehydration. In a large number of tests, the ratio, fresh volume: dry volume, was 1.411. Formulas are deduced for calculation of green weight of skins.

Artanol WL. By M. Schwank. *Ciba Rev.,* No. 87, 3125 (1951). Through *Brit. Abstr. BII,* 946 (1951). This is a water soluble melamine resin which is an excellent self-tanning agent. Artanol WL condenses in weakly acid solution and deposits on the hide fibers. There is also a chemical union between the resin and fibers. The limed and bated hides may be drummed in a neutral liquor with 10 per cent Artanol WL until penetration is complete, about 1-4 hours, then 1-2 per cent formic acid is added gradually to start the tanning. Alternatively, thinner hides are drummed in a weakly acid aqueous solution containing 5 per cent salt and 10 per cent Artanol WL. This resin is particularly suitable for mixed tanning. Hides pretanned with 3 per cent Artanol WL can then be tanned with vegetable or synthetic agents. Artanol WL can be used at any stage of the chrome tanning process. Good quality leathers for various purposes are obtained by modification of these methods.

Sapamine CH and KW in the Leather Industry. By M. Schwank. *Ciba Rev.,* No. 87, 3128 (1951). Through *Brit. Abstr., BII,* 945 (1951). These cationic auxiliary products are chiefly used in the leather industry as a pretreatment, to deepen the shades of acid or direct dyes on combined tannages and chrome-syntan leather. They are also satisfactory for wetting back dry alum tanned gloving leathers and chrome suedes, especially if they are to be dyed in full, strong shades. Sapamine CH and KW do not exert a reserving effect on acid and direct dyes. Dry, dyed, and wheeled suede leathers are sprayed with a solution of 5 g. Sapamine KW in 250 cc of ethyl alcohol and 750 cc. of water to obtain improved handle, fastness to rubbing, and depth of shade. These agents impart a greasy handle to most leathers, which is often desirable and obviates seasoning.

Effect of pH on Behavior of Tanning Solutions Towards Salting Out. By G. d'Orsi. *Boll. Staz. sper. Industr. Pelli, Mater. concianti*, **27**, 125 (1951). Through *Brit. Abstr. BII*, 1051 (1951). The precipitability of extracts of quebracho, chestnut, and sumac is found by adding 11, 22 and 32 per cent aqueous salt, and weighing the tannin precipitate. Effects of salt at constant pH are those found by Stiasny and Salomon, but salt values agree with astringency values quoted by Crede. Tannin precipitation increases as pH increases. The effects of pH are greater at lower salt value.

Service Tests of Boys' Shoes. By R. B. Hobbs. *Amer. Shoemaking*, Feb. 6 and 13, 1952. Tests of 120 pairs of boys' Goodyear welt shoe in actual service indicate the following tentative conclusions. They should not, in general, be extended to other classes of footwear, since boys usually wear shoes more severely and for a shorter time than any other large group in the civilian population. Chrome retan upper leather is more resistant to scuffing than the customary chrome "elk" upper leather. An upper leather made with a resorcinol syntan is very promising, as it has the flexibility desired for children's shoes, with good resistance to scuffing. Uppers without back seams were superior to conventional uppers in reducing the breakdown of the rear part of the shoe.

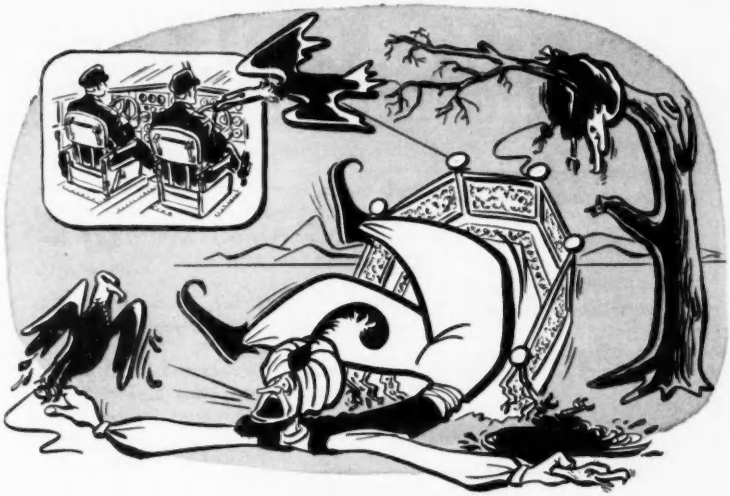
Each of the commonly used sole materials seems to have a defect that needs improvement. Corded rubber soles failed to hold stitches adequately; styrene-butadiene resin soles showed excessive expansion or creep, with resultant separation from the shoe bottom or curling of the entire bottom; and leather soles lacked adequate resistance to abrasion. Rubber heels of the quality customarily used on boys' shoes did not appear to be sufficiently durable to match the quality of the soles. Leather counters seemed to be somewhat more durable than fiber counters, but either would be satisfactory if the shoes are treated with reasonable care. Chrome retan insoles appeared to be slightly better than vegetable insoles, but either should be satisfactory for boys' shoes. Lining fabric treated with a resin was no more durable than untreated fabric for the short period that these boys' shoes were worn. There was no perceptible difference in the behavior of thermoplastic and solvent-activitated box toes. Flexible wooden bottom filler distributed the wear more evenly over the width of the outsole, and may result in some increase in durability of the sole.

PATENTS

Tanning and Sizing Leather. Brit. Pat. 617,598. V. Weinberg. July 20, 1945. Improved oils, sizes, tanning agents, printing inks and like materials suitable for treating proteinic and cellulose substances, e.g., fibres, leather, paper, cardboard, etc., are obtained by incorporating in the oils, etc. (a) synthetic resins or (b) the monomeric constituents of synthetic resins which latter are then formed in situ in the treated material, by means of a "carrier" comprising an oil soluble mahogany sulphonic acid which is obtained in the refining of mineral oils and which is soluble in alcohols, aliphatic, and aromatic hydrocarbons. The sulphonic acid may also be prepared synthetically. In addition to the carrier so-called "linkage agents" may be employed, i.e., mutual solvents of the added and treated materials, e.g., aldehydes, ketones, esters, phenols. Specified resin-forming monomers are phenols, ureas, sulphonamides, amines, amides, aldehydes and ketones; plasticizers, filters and catalysts may be added, e.g., waxes, starches, dextrin, glue casein; synthetic rubbers and rubber; organic cyanates. In examples (1) a solution suitable for application by spraying comprises a mixture of styrene, ethyl alcohol, benzoyl peroxide and an oil soluble sul-

phonate; (2) sole leather is "oiled off" by a mixture comprising β–naphthylamine, furfural, refined coal tar oil, benzene, sulphated fish oil, oil soluble mineral oil sulphonate, condensation taking place in the customary drying process; (3) 1 mol urea and .75 mol formaldehyde are dissolved in 500 per cent of a solution of a sulphated oil and the solution is used for brushing on to formaldehyde tanned leather.

Filling Leather. Brit. Pat. 618,847. D. B. Kelly, J. H. Sharphouse, and Imperial Chemical Industries. Nov. 18, 1946. Leather is filled by subjecting hides and skins to a tanning operation in conjunction with a treatment with an aqueous dispersion of polythene. The treatment may be effected before or after tanning. According to one example depickled New Zealand sheepskins as pH 5-7 are treated with a 30 per cent aqueous dispersion of a polythene of softening point 110°C. and viscosity at 190°C. of 3,500 poises repickled and chrome tanned. In another example rough tanned East Indian sheepskins after stripping in a solution of sodium bicarbonate and washing are treated with a dispersion of a polythene similar to the above and subsequently chrome tanned.



NOTHING LIKE IMPROVEMENT!

...and the "Double Action" **New NOPCOLENES**

bring you improvement ***PLUS***

King Kai Kaoos of ancient Iran was not only heir-minded but air-minded. When local engineering talent came up with a neat ivory platform powered by eagles eager to get at food suspended out of reach above them, Kai, himself, went up. But when the eagles tired of working for nothing, Kai came down—and hit hard, barren ground.

How different today, with thousands of horsepower at the command of well-fed pilot and co-pilot! Here's double-action improvement on a royal scale.

Reminds us of Nopcolenes. Our original Nopcolenes started with a flight of creative imagination: we believed we could produce *double duty* tanning oils that would give excellent surface lubrication *plus* easily controlled penetration. Our original Nopcolene* products showed conclusively that we were on the right track, but they did not attain the performance peak we sought. However, we researched further, with the result that today's *improved* Nopcolenes are truly sensational fatliquors—enabling the tanner to obtain any degree of surface feel, hand, break, and stretch he requires.

Unlike King Kai, today's tanner who uses the improved Nopcolenes strikes pay-dirt—in the form of better products, increased sales, and *extra* customer goodwill.

Send for our free book giving details about the new double-action Nopcolenes, plus formulas for various leathers.

Nopco Oils Make Good Leather Better

NOPCO
EVOLVED THRU RESEARCH

NOPCO CHEMICAL COMPANY, Harrison, N. J.

Branches: Boston • Chicago • Cedartown, Ga. • Richmond, Calif.

*T. M. Reg. U. S. Pat. Off.

CALAFENE
Binder and Filler

PIGMENT FINISHES Uniform quality binder, filler and carrying agent. Builds up body. Improves covering power and spread. Nourishes fiber and eliminates harsh feel. No manipulation necessary.

LEATHER FILLER Imparts permanent flexibility. Does not "pipe" or crack. Covers cuts and imperfections.

SUEDE SPLITS Plumps the skins, strengthens and builds up low ends. When sueded the skins have a velvety nap and full mellow feel. Does not lay on the surface.

APEX
MARK of QUALITY

Established 1900
Apex Chemical Co., Inc.
225 West 34th St., New York 1, N. Y.

Manufacturers of a complete line of specialties for the tanning trade

UNION TANNERS SUGAR CHIPPED OR BILLETS
UNIFORM CLEAR NON-FOAMING UNIFORM CLEAR
CHIPPED OR BILLETS UNION TANNERS SUGAR
NO NG
UN ETS
UN AR
CH AR
NON-FOAMING UNIFORM CLEAR NON-FOAMING
UNION TANNERS SUGAR CHIPPED OR BILLETS
UNIFORM CLEAR NON-FOAMING UNIFORM CLEAR

UNION STARCH & REFINING CO.
Established 1903
General Offices: COLUMBUS, INDIANA

TYPICAL ANALYSIS OF BARIUM'S

SODIUM SULPHIDE FLAKES

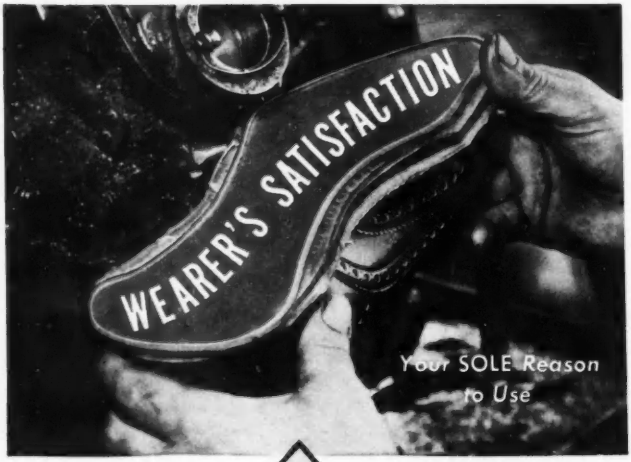
Fe	0.0005%
Other Heavy Metals	Nil
Na Cl	0.40
Other Na_2O (not oxidizable)	1.35
Na_2S	61.00

Manufactured in large tonnages by

BARIUM REDUCTION CORPORATION

SOUTH CHARLESTON 3, WEST VIRGINIA

need we say more?



DIAMOND A COMPOUND

TESTED and proved for 40 years—Diamond A is recognized as the Tanners' standard sponging and washing compound.

Here's why. Diamond A does a *double* job — (1) It prepares sole leather for rolling and protects the grain. (2) Used as a dip after rolling, it toughens the grain and improves color and finish.

Why delay? Let the Borne, Scrymser representative give you full particulars on Diamond A. You'll agree it's in a class by itself.

OTHER BORNE, SCRYMSER SPECIALTIES
(Get the Facts about These, Too!)
P COMPOUND for WHEELING
A COMPOUND for SPONGING
Supreme A Compound
Bretolene • Saxon Oil

BORNE SCRYMSER Since 1874
Our Laboratory Facilities are always at your disposal

BORNE, SCRYMSER COMPANY Elizabeth, N. J. Charlotte, N. C.

Warner

BELL-MINE LIME

Year-round Uniformity
Dependable Source of Supply

WARNER COMPANY

Bellefonte Division, Bellefonte, Pa.

PITTSBURGH - - - - PHILADELPHIA - - - - NEW YORK

THE OHIO LEATHER CO.

LUXOR CALF COLORS BLACK JETTA CALF
WASHETTE • WHITE AND COLORS

TANNERY & GENERAL OFFICES: GIRARD, OHIO
BOSTON • NEW YORK • ST. LOUIS • CHICAGO

EISENDRATH FINE CALF LEATHERS

IN COLORS AND BLACK

B. D. Eisendrath Tanning Company

801 Merchandise Mart, Chicago, Ill. • Tannery at Racine, Wisconsin

195 South St., Boston, Mass., Day Gormley Leather Co. 12 E. 33rd St., New York City, Moe Shapiro

Always Foremost

Armour's QUALITY Leathers USA

Sole and Upper Leather

•

ARMOUR LEATHER CO.

Chicago Boston New York

BORAX AND BORIC ACID HAVE LONG BEEN USED IN THE TANNING AND FINISHING OF GOOD LEATHER

When you want **BORAX**

or want **BORIC ACID**

Think first of **PACIFIC COAST BORAX CO.**

DIVISION OF BORAX CONSOLIDATED, LIMITED

NEW YORK • LOS ANGELES • CLEVELAND • CHICAGO

Distributors located in principal cities throughout the U.S.A.

MANUFACTURERS OF FAMOUS "20 MULE TEAM" PACKAGE PRODUCTS

REILLY-WHITEMAN-WALTON CO.

OILS of CHARACTER

CONSHOHOCKEN, PA.

THE LEATHER MANUFACTURER

ESTABLISHED 1883

Exclusively a Tannery Paper

Devoted to Leather Technology, Tanning and Finishing of Leather, Tannery News and Markets.

Affords complete tannery coverage, concentrated among tanners, chemists and buyers of materials, raw stock and equipment.

Technical articles and newsworthy features invited for publication.

THE LEATHER MANUFACTURER

NEW YORK OFFICE
171 William St.

BOSTON OFFICE
683 Atlantic Ave.

Where Coverage Counts!

Shoe and Leather REPORTER

TANNERY BUYER

THE TECHNICAL JOURNAL FOR SUPERINTENDENTS, CHEMISTS, TANNERS AND BUYERS

Now more popular than ever! **Shoe and Leather Reporter's** TANNERY BUYER Section, published in the third issue of every month, is read by every important executive, superintendent, chemist, and buyer. It has coverage where coverage counts!

Shoe and Leather
REPORTER
Representatives in

Boston (Hdqtrs)	Washington
Chicago	St. Louis
New York	London, Eng.
Philadelphia	Los Angeles

San Francisco

SHOE AND LEATHER REPORTER
210 Lincoln Street, Boston, Mass.

Salem Oil & Grease Co.

FAT LIQUORS

FEATURING

CONTROLLED PENETRATION

●

SALEM, MASSACHUSETTS

STANDARD HIDE POWDER

A material made to specifications and used internationally for the analysis of vegetable tanning materials

FRANK F. MARSHALL
RIDGWAY · PENNSYLVANIA

Garden State Tanning Inc.
Pine Grove, Pa.

Manufacturers of
Upholstery Leather

New York Office 330 Fifth Avenue

TANOLIN®
Best Known—Most Used
One-Bath Chrome Tan
Manufactured by
THE MARTIN DENNIS COMPANY
Newark, N. J.
DIAMOND ALKALI CHEMICALS
Division of Diamond Alkali Company

KEPEC FINISHES · KCC CHEMICALS

KEPECO FINNALINE KEPOLAC
EMULLO FRESKO FONDO
RICCOTAN UNI-LAK
(Reg. U. S. Pat. Office)

KEPEC CHEMICAL CORPORATION
Milwaukee 1, Wisconsin

A.C.T. TRASK TRADE MARK

ARTHUR C. TRASK CO.
Tanners Oils & Extracts
CHICAGO, ILL.
4103 S. LASALLE ST.

. . . . . LET'S GET THE **ANSWERS ABOUT** MAGAZINE **LEADERSHIP** *in the Tanning Industry...*

Which magazine does the outstanding job in editorial service?
Which magazine has 101% more paid and audited circulation?
Which magazine carries more than 100% more advertising?

Tanning industry executives know that only in Leather and Shoes do they get the complete and timely job in news, markets, features, and editorial service.

Complete and often *exclusive* coverage of technological progress in tanning methods and production, supplies, materials, equipment and machinery, *plus* the facts about demand, markets, uses, and trends in the leather-using division of the industry, *plus* the keenest, most thought-provoking editorials on the leading problems and interests of the entire field.

Because they get the fullest measure of service each week, tanning executives subscribe to L & S at a 100% higher rate than to the second paper —almost 2 to 1 leadership.

This leads naturally to greater productivity for advertisers who respond with the greatest volume of advertising. L & S carries 124% more tanning material, chemical, oil, etc., advertising than the second paper, and 117% more tanning machinery and supply advertising.

That's the story about magazine leadership in the tanning industry. It's L & S all the way. If you want more facts, write us today.

L&S

LEATHER AND SHOES
300 W. ADAMS STREET
CHICAGO 6, ILLINOIS

Finishes
for all types of
Leather

NEWARK
LEATHER FINISH CO.
8 WILHELM ST. HARRISON, N. J.
Telephone: Humboldt 5-3470

DYESTUFFS **DYEWOODS**

CHEMICAL SPECIALTIES

▼

COMMONWEALTH COLOR AND CHEMICAL CO.
Main Office, Factory and Laboratories
3240 GRACE AVENUE NEW YORK 67, N. Y.
Philadelphia - Chicago - Gloversville Montreal

Barkey Importing Co. Inc.

44 East 53 St., New York 22, N. Y.

IMPORTERS

Vegetable Tanning Extracts and Raw Materials

Wattle Bark
Wattle Extract
Quebracho Extract
Valonia Cups, Beards
Valonia Extract, Valex Brand
Mangrove Bark
Sicily Sumac
Myrabolans
Divi divi

SOLE AGENTS FOR UNITED STATES AND CANADA
for
Italian Chestnut Extracts
Solid and Powdered

Produced by
S. A. LEDOGA
MILANO, ITALY

PRESTO COLOR COMPANY
ESTABLISHED 1918
CUDAHY, WIS.

Dry Colors — Leather Finishes

MORITE BRAND
Sulphonated and Compounded
OILS
EST. 1908 EST. 1908
WHITTEMORE-WRIGHT COMPANY, INC.
62 ALFORD ST. CHARLESTOWN DISTRICT BOSTON, MASS.

HOWES LEATHER CO. INC.
SOLE LEATHER
•
Tanners Cut Sole Division
•
CUT SOLES
BOSTON, MASS.
ST. LOUIS, MO CHICAGO, ILL.

BONA ALLEN, INC.
Buford, Georgia
TANNERS SINCE 1873
•
Finest English Rein and Strap Leather
Latigotan Harness Leather
Manufacturers of genuine English type and full rigged hand tooled roping saddles.

"The Extension of Knowledge is by the Investigation of Matter".

This space dedicated to
Tanners' Council Research Laboratory
by a Friend

RESEARCH
has Two functions
To produce a better Product and to do it More Economically.

THE TANNERS' COUNCIL RESEARCH LABORATORY
UNIVERSITY OF CINCINNATI

THE TANNERS' COUNCIL RESEARCH LABORATORY
University of Cincinnati

We serve the Tanning and Leather Industry through a broad program of Research.

RESEARCH PAYS DIVIDENDS
when Properly Applied.

RESEARCH LABORATORY THE TANNER'S COUNCIL
Universtty of Cincinnati

WHEN
YOU
BUY
TANNERS'
CORN SUGARS
CORN SYRUP
CORN STARCH
LACTIC ACID
REMEMBER

CLINTON

CLINTON FOODS INC.
CLINTON, IOWA

BORNEO **CUTCH** EXTRACT
(MANGROVE BARK EXTRACT)
SAXE CUTCH CORPORATION
500 FIFTH AVENUE NEW YORK 36, N. Y.

UNIFORM TANNER'S OILS
for Every Type of Leather
MARDEN WILD CORPORATION
SOMERVILLE, MASSACHUSETTS
MARDEN WILD OF CANADA, LTD., HALIFAX, N. S.

LONGER-WEARING LEATHER

Many leather chemists agree that longer-wearing leather is produced by use of Sun's "Job Proved" Leather-Processing Oils. These oils provide fiber lubrication. They also contribute to the even distribution of the natural oils and greases in the hide. They produce an even, light color. They mix easily. For additional information, call your nearest Sun Office . . . or write to SUN OIL COMPANY, Philadelphia 3, Pa. *In Canada:* Sun Oil Company, Ltd., Toronto and Montreal.

SUN PETROLEUM PRODUCTS SUNOCO
"JOB PROVED" IN EVERY INDUSTRY

THE
TANNERS' COUNCIL RESEARCH LABORATORY

at

THE UNIVERSITY OF CINCINNATI

is

THE DEPARTMENT OF BASIC SCIENCE

in

THE GRADUATE SCHOOL OF ARTS AND SCIENCE

The purpose of the laboratory is to conduct scientific research in the fields of Science concerned with Tanning and Leather.

To train Chemists in the technique of research and prepare them for Industry.

This Laboratory serves as the Official Technical Headquarters for the Tanning Industry of the United States.

Your inquiries will be gladly answered.

Address DR. FRED O'FLAHERTY, Director
Tanners' Council Laboratory
University of Cincinnati
Cincinnati 21, Ohio.

FOR VEGETABLE TANNED SOLE LEATHER

THE BEST

BESCO

COMPOUNDS

FOR CHROME CHROME RETAN SOLE LEATHER

TANNERS' SUGAR **LACTIC ACID**

BUFFALO EXTRACT & SUPPLY CO. -:- BUFFALO, N. Y.

«Buy More Bonds»

A New Addition To The Family

As one of the largest producers of Sulfuric Acid for well over a quarter of a century, naturally our initial interest in organic chemicals is centered around ORGANIC SULFONIC ACIDS and their derivatives. Intensive research has developed a new approach to this basic reaction and a new plant employing a revolutionary Sulfonation process is under construction.

Pilot plant quantities of many unusual Sulfonates are now available. We are particularly interested in tough or unusual sulfonation reactions.

Call, wire or write us. Perhaps we can solve your problems.

ORGANIC CHEMICALS DIVISION

TENNESSEE CORPORATION

619 Grant Building, Atlanta, Georgia

TANNERS! Now Available . . .

REQUESTED SHORT TERM COURSES

IN SPECIFIC PHASE STUDIES

COLORING
FAT LIQUORING
FINISHING

Especially designed for industry personnel; includes Beamhouse work.

FIRST COURSE COMMENCES SEPTEMBER 17TH

ALSO

REGULAR LONG TERM PROGRAMS — 3 Terms for High School Graduates; 2 Terms for College Graduates

Sponsored by Tanning & Allied Industries • Approved by Tanners' Council of America, Inc.

SCHOOL OF LEATHER & TANNING TECHNOLOGY

PRATT INSTITUTE • BROOKLYN 5, N. Y.

Write for literature and application form.

Fill in and Mail →

NAME .....

ADDRESS .....

CITY & STATE .....

«Buy More Bonds»

INDEX TO ADVERTISERS

AMERICAN CYANAMID COMPANY V
AMERICAN DYEWOOD CO. X
AMERICAN EXTRACT CO. ..... Outside Back Cover
APEX CHEMICAL CO., INC. XXIV
ARKANSAS COMPANY, INC. VI
ARMOUR LEATHER CO. XXVIII
ARTHUR C. TRASK CO. XXXI
ARTHUR THOMAS CO. XXII
ATLAS REFINERY XVI
BARKEY IMPORTING CO., INC. XXXIV
BARIUM REDUCTION CORPORATION XXV
BONA ALLEN, INC. XXXV
BORNE SCRYMSER COMPANY XXVI
BUCKMAN LABORATORIES, INC. XVIII
BUFFALO EXTRACT & SUPPLY CO. XXXVIII
CHEMTAN COMPANY XXI
CLINTON FOODS, INC. XXXVI
COMMONWEALTH COLOR & CHEMICAL CO. XXXIII
EISENDRATH TANNING CO. XXVII
FRANK F. MARSHALL XXXI
GARDEN STATE TANNING INC. XXXI
GENERAL DYESTUFF CORPORATION IX
HADLEY BROS. - UHL COMPANY VIII
HOOKER ELECTROCHEMICAL CO. XIX
HOWES LEATHER CO., INC. XXXV
INTERNATIONAL PRODUCTS CORP. XII
KEPEC CHEMICAL CORPORATION XXXI
LEATHER AND SHOES XXXII
LEATHER MANUFACTURER, THE XXIX
L. H. LINCOLN & SON, INC. VII
MARDEN WILD CORPORATION XXXVII
MARTIN DENNIS CO., THE XXXI
MEAD CORPORATION, THE XIII
NEWARK LEATHER FINISH CO. XXXIII
NOPCO CHEMICAL CO. XXIII
OHIO LEATHER CO., THE XXVII
OLSON SALES AGENCY, THE ..... Inside Front Cover
PACIFIC COAST BORAX CO. XXVIII
PRESTO COLOR CO. XXXV
REILLY-WHITEMAN-WALTON CO. XXIX
RIVER PLATE IMPORT AND EXPORT CORPORATION, THE XX
ROBESON PROCESS CO. II
ROHM & HAAS XV
SALEM OIL & GREASE CO. XXX
SAXE CUTCH CORPORATION XXXVII
SCHOOL OF LEATHER & TANNING TECHNOLOGY XL
SHOE & LEATHER REPORTER XXX
SOCONY-VACUUM OIL CO. I
SOLVAY SALES DIVISION, ALLIED CHEMICAL & DYE CORP. XI
SUN OIL COMPANY XXXVII
TANEXCO, INC. ..... XLII—Inside Back Cover
TANIMEX CORPORATION XVII
TANNERS' COUNCIL RESEARCH LABORATORY ..... XXXVI—XXXVIII
TEAS EXTRACT CO. III
TENNESSEE CORPORATION XXXIX
UNION STARCH & REFINING CO. XXIV
WALLERSTEIN COMPANY, INC. IV
WARNER CO. XXVII
WHITTEMORE-WRIGHT CO. XXXV
WOLF, JACQUES & CO. XIV

CHESTNUT

ITALIAN EXTRACT

highest quality — made under
the supervision of the world's
leading extract chemists

Cipec Brand

TYPICAL A.L.C.A. ANALYSIS

	Solid	Powder	Spray Dried
TANNIN	61.72	66.7	73.5
NON-TANNIN	21.65	21.2	19.1
INSOLUBLES	.65	.6	.7
WATER	15.98	11.5	6.7
ASH	.67	.82	.75

Clean Light Color — Smooth Silky Grain

For further information address:

TANEXCO, INC.

549 W. Washington Blvd. **Chicago 6, Illinois**

SOLE AGENTS
U. S. A.

MYRTAN

A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

TANNIN	61.55
NON-TANNIN	16.03
INSOLUBLES	1.70
WATER	20.72

Also Available as Liquid with 30% Tannin

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

For further information address:

TANEXCO, INC.

549 WEST WASHINGTON BLVD., CHICAGO 6, ILLINOIS

SOLE AGENTS
U. S. A.

DERMABATE COMPOUNDS LIQUID EXTRACTS

HEMLOCK
OAK
MANGROVE
WATTLE
STAINLESS SUMAC
ORDINARY SUMAC
QUEBRACHO
SPECIAL DIPPING EXTRACTS
RAPID TAN "G"

★

AMERICAN EXTRACT CO.

Manufacturers of the Largest
Variety of Vegetable Tanning Extracts
Established 1887
PORT ALLEGANY, PA.

CANADIAN REPRESENTATIVES:
McArthur Chemical Co., Ltd., 20 St. Paul St., West, Montreal: 73 King St., West Toronto
ENGLISH REPRESENTATIVES:
Roy Wilson, Dickson, Ltd., 7-9 Railway Approach, London, S. E. 1